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MEMORIAL LECTURES

DELIVERED BEFORE

THE CHEMICAL SOCIETY

1901—1913

BY

Sir Henry A. Miers.
Professor J. H. Van't Hoff.
Professor W. H. Perkin.
Sir Edward Thorpe.
Professor F. Wigglesworth Clarke.
Sir William A. Tilden.
Professor H. B. Dixon.
Sir William Ramsay.
Sir Oliver Lodge.
Professor J. Walker.
Professor F. S. Kipping.

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P. Ramsenberg

MEMORIAL LECTURES

DELIVERED BEFORE

THE CHEMICAL SOCIETY.

RAMMELSBERG MEMORIAL LECTURE.

(Delivered on December 13th, 1900).

By H. A. Miers, M.A., D.Sc., F.R.S., Waynflete Professor of Mineralogy in the University of Oxford.

The Chemical Society has recently become only too familiar with the death of foreign members of patriarchal age, otherwise it would be difficult to realise that a chemist whose death took place last year was the friend and associate of Berzelius. The man whose life and work we commemorate to-day was an almost exact contemporary of another famous chemist whose great genius and high character have been recently depicted for us by his friend and fellow-worker. Rammelsberg was born two years later than Bunsen and outlived him by less than one year.

Among the workers who during this period contributed to raise the edifice of modern chemistry upon the foundations laid during the childhood of these two men, some, like Bunsen, were thinkers of the highest genius whose inspiring ideas directed the development of the structure, others, like Rammelsberg, were the skilful and indefatigable craftsmen who amassed and set in order the material. Owing to the fact that Rammelsberg's name is not associated with any of the great discoveries of a period which belongs mainly to organic chemistry, and that he purposely confined his life-work to inorganic research, there is some danger lest the value of his contributions to science should be underrated, except, indeed, among mineralogists; I am, therefore, particularly glad to have this opportunity of sketching a brief record, however imperfect, of his colossal labours. It will be made clear, I

hope, that, although brought up in the school of Berzelius, Rammelsberg was by no means one who ignored the progress of the modern chemistry, but did, in fact, contribute in no small degree to its dissemination. To those among the younger generation of organic chemists who know anything of his work, the name of Rammelsberg will, I imagine, evoke the recollection of a vast number of papers whose titles relate to mineral and other inorganic analyses and to crystallographic measurements; they may only know him as a patient worker and think of him as one who pursued his labours undisturbed by the growth of modern chemistry. This would be a very false estimate, and in order to dismiss such a misconception at the outset, I cannot do better than quote the words addressed to Rammelsberg on the occasion of his Doctor's Jubiläum, I believe by Hofmann, on behalf of the Berlin Academy of Sciences. After describing his labours in practical chemistry, he says, "It was not only the empirical but also the theoretical side of science which attracted your lively attention. Originally brought up in the school of Berzelius, and the contemporary of Heinrich and Gustav Rose, of Mitscherlich and Wöhler, you subsequently witnessed all the changes which chemical theory has experienced up to the present day. With a quick eye you recognised early the advantages of the present views and *you were among inorganic chemists the first to adopt the new system of formulæ.*"

While I am glad that it has fallen to my lot to recall these features of his life-work, I regret that I never had the opportunity of even seeing the man whom I have to describe. Whatever impression of his life and work I may succeed in conveying is derived solely from a study of his publications or from the reminiscences of others to whom he was personally known; and he was a man who more than any other led the uneventful laborious life of a student.

Among the day dreams to which most persons have yielded, is the fascinating speculation as to what would have been their lot had their life been set in earlier times. Could any chemist choose for himself a more attractive period than the early part of the nineteenth century, when the influence of Berzelius had entered into the heart of the science? In the youth of Rammelsberg, the electro-chemical theory had overcome all opposition and supplied a great principle of apparently universal application; the modern methods of analysis were being perfected; and the chemist was for the first time really equipped for conquest in the fields of research. It is a commonplace of historical criticism that in the early history of any art there is a period when the materials, the instruments, and the methods have just been matured, although the art has not become self-conscious; when the artist revels in his newly-acquired powers, and finds a pleasure in the exercise of the chisel or the brush without any thought of whither

his work tends or what purpose it is to serve. Something analogous happens, I think, in the early history of a science, and at the time when Rammelsberg began to work, a chemist must have felt that every analysis which he could make, every substance which he could prepare, was something new, of unknown import, and involved the exercise of new powers. To a young, ardent, and ambitious student, this in itself must have been an overpowering impulse to energetic labour; in no life is this delight in work better exemplified than in that of Rammelsberg.

Karl Friedrich Rammelsberg was born on April 1st, 1813, at Berlin. He was of humble origin, and was entirely a self-made man; his family came from Altenbrak an der Bode in the Harz; his father was in quite a small way of business in Berlin. As a boy he was educated in a private school, and in the Friedrich Werder Gymnasium; he then entered the Realschule, in the Kochstrasse, where he seems to have received some little scientific training from the director, Spillecke. Here he remained for four years, and leaving at the age of 15 entered the Koch Apotheke, where he studied for the next four years, with the view of becoming an apothecary. In this Apotheke he seems to have learnt botany from Hayne and pharmaceutical chemistry from Heinrich Rose; under the latter, Rammelsberg must have first become acquainted with the spirit of scientific research, and he himself says that he never forgot the teaching of this man, from whom he received such varied and valuable assistance. In 1832, at the age of 19, he obtained a place in the Apotheke at Dardesheim, near Halberstadt. After remaining there only one year, the young chemist took the step which determined his whole future career; he suddenly abandoned the line of life upon which he had entered, and returned to Berlin with the object of obtaining a university education and devoting himself to pure science; this step was probably taken by Rose's advice: it must have required great determination for a lad of his education and antecedents to enter this new world, and compete for the distinctions gained by men of the calibre of Mitscherlich and Heinrich Rose. In order to pass in the necessary examinations in Latin and Greek, he was obliged to teach himself unaided the latter language. This was accomplished at odd moments and in the intervals between other studies. In 1834, he was able to pass his Maturitätsexamen at the Gymnasium zum grauen Kloster, and was matriculated. Erman and Magnus were at this time the professors of physics, Mitscherlich and Heinrich Rose of chemistry, Weiss and Gustav Rose of mineralogy; with all these he worked, as well as with Hoffmann in geology. His Arbeit was carried out in Mitscherlich's laboratory and was a dissertation entitled "De cyanogenii connubiis nonnullis" (1837). The titles of his four doctoral theses are interesting in the light

of the researches to which he devoted the remainder of his life; they were entitled:

(1) Experientia chemica in constituendis theoriis geologicis praecipue est observanda.

(2) Connubia chemica organica et inorganica haud absolute discerni possunt.

(3) In systematibus, quæ hucusque exstiterunt, chemicis theoria deflagrationis summum tenet locum.

(4) Systema mineralogicum *naturale* neque indolem externam neque internam fossilium negligere debet.

A man's early work is generally a clue to his subsequent tendencies, and Rammelsberg's theses are no exception; his interest in inorganic chemistry and in substances like the cyanides, which lie on the borderland between the organic and inorganic; his leaning towards the geological aspects of chemistry; his life-long study of both the chemical composition and the crystalline form of minerals, are all foreshadowed in these titles.

Three years later he began to teach at the Hochschule; in 1841, he was "habilitated" as Privatdocent at the university, and was also a teacher at the Handels-Schule.

At the age of 24 (in 1837), he had already begun to publish analyses of inorganic compounds and minerals—the opening of a long series of researches in inorganic chemistry and mineralogy, many of them lengthy and laborious memoirs, which issued in an unbroken stream from 1838 to 1888.

When he became Privatdocent there were only two laboratories in Berlin where a student could work, namely, those of Heinrich Rose and Mitscherlich, and in these only a few specially recommended pupils could find a place; Rammelsberg, therefore, with characteristic energy, started a private laboratory of his own in which all his earlier pupils must have obtained their experience; it was so small that only two students could be accommodated at a time, and when one pair went off a second pair came on; the fee was the ridiculously small one of 50 pfennigs. With this scanty help, he was also able to assist his mother to support herself.

This small beginning was really the initiation of practical laboratory instruction in Berlin, and was the seed from which sprang the second chemical institute of which Rammelsberg was ultimately made the first director. His time must have been very fully occupied, and yet not only did the publication of scientific papers continue unabated, but he began to add to them the first of a series of text-books and of monumental works of reference: in 1841 his dictionary of chemical

mineralogy, in 1842 his text-book of stochiometry and theoretical chemistry. In a very short time he became a recognised authority on chemistry, mineralogy, crystallography, and metallurgy.

In 1846, he was appointed Professor extraordinarius of inorganic chemistry, and in 1850 he was also made instructor in chemistry at the Gewerbe-akademie, where he was at last provided with an adequate chemical laboratory ; this academy ultimately developed into that splendid institution, the Technische Hochschule of Charlottenburg. He was also instructor at the Mining Academy from the time of its foundation in 1860. In 1855, he was made a member of the Berlin Academy.

It was not until 1874 that Rammelsberg attained the full recognition of his labours and was made ordinary Professor of inorganic chemistry (in succession to Heinrich Rose), a position to which he had raised himself from a lowly origin and by the exercise of the most extraordinary industry.

In 1846 he married the daughter of a man well known in the history of mineralogy, Oberbergrath Zincken, of Mägdesprung.

He took an active part in the foundation of the Berlin Chemical Society in 1868, and was its President in 1870 and 1874.

From the impression which I have derived from those who knew him, he must have been a man of unusually short stature, energetic carriage, and somewhat austere manner ; an early photograph represents, by the sharply-cut features, the keen eye, and the compressed lips, a man of precision and determination ; he was clear and concise as a lecturer ; a very quick but accurate worker ; sharp in exposing the mistakes of others, but equally ready to learn from them and correct his own errors.

Professor Liveing, who worked in his laboratory at the Gewerbe-akademie in 1852, kindly allows me to quote his recollection of that period. He regards Rammelsberg's asperity of manner as due to his "habit of expressing himself in few words ; words, however, which were always to the point, and expressed his meaning clearly." "He gave me the impression," he says, "of having a mathematical mind, and of being very accurate. His laboratory was, by comparison with those of the present date, a makeshift one ; nevertheless, good work could be done there, but the appliances required for a research had, for the most part, to be extemporised. He was, however, more ready than many to adopt improved methods and apparatus. When I first went to his laboratory we had no gas, and had to use spirit lamps, and charcoal braziers for heating, but while I was there he introduced gas and other improvements ; and I well remember that Mitscherlich remarked to me that so doing was a mistake, because the greater part of Rammelsberg's pupils would be dispersed in after life in places

where they could not get gas, and would find themselves in difficulty because they could not command the resources they had learnt to depend on. Another point about him was that he did his work himself. He had no assistant in research when I was with him. He had, of course, some of the more advanced students who acted as demonstrators to the younger ones, and he used the results which his pupils obtained as checks to his own work, but that work, so far as I saw, was essentially his own. How it may have been afterwards I cannot say, but I think it was in his character to be very independent, and more desirous of doing good than of making a great show. He may have been a disappointed man; his manner rather suggested that, and his way of speaking of some of his contemporaries was perhaps a little cynical."

It must be remembered that the time of which Professor Liveing writes was twenty years before Rammelsberg's labours were crowned with full recognition on the part of the university, and it is pretty certain that his rising claims for a long time met with constant opposition in Government circles. On the other hand, he was by no means a man whose efforts were directed to personal advancement, and whether he met with promotion or neglect, assistance or opposition, he was inspired by a single-hearted devotion to science, which impelled him to unremitting labour and research.

Private appreciations and reminiscences are always more impressive and trustworthy than such as are written for publication, and I am glad to have the permission of Professor Wolcott Gibbs (himself now one of our oldest foreign members), who was his pupil in 1845, to quote from a letter which he wrote to his old teacher forty years afterwards. "Many, many years have passed since I entered your laboratory as a pupil, but I well remember the pleasant afternoons that I spent with you, and the kind and friendly interest which you showed in my instruction. The very room is fresh in my mind's eye, and I remember the names of the three Greek students who were my fellow pupils. Since then, your own noble example of earnest, constant work has always been before me. Of the many noble men whom I learned to know in Berlin, you, I believe, alone remain; Poggendorf, Heinrich and Gustav Rose, Magnus, Dove, Riess, Johannes Müller, have gone. You presented me to Berzelius on the day of the dinner to him, and I sat next to you at table, when you spoke so well 'im Namen der jüngeren Chemiker.' In all these years the memory of my first teacher in analytical chemistry has always been cherished."

With reference to this occasion and the memorable visit of Berzelius, Professor Wolcott Gibbs writes to me: "Many German professors and chemists and physicists were present. Among them Jacob Grimm. Several speeches had been made, when Rammelsberg asked me how

they compared with speeches made on similar occasions in America. I told him they were admirable, but wanted what the French call *verve*, life and spirit. Then Rammelsberg rose, and made a more spirited speech, which was very well received."

His skill as a *raconteur* is vividly in the minds of those who remember those happy days of the Berlin University, when professors and students met together on terms of equality, and the latter had the opportunity of hearing the conversation of perhaps the most brilliant intellectual society in Europe. Among those who entertained each other with reminiscences in the informal evening gatherings after the meetings of the Geological Society, none could be more interesting than Rammelsberg.

His scientific character, I think, may be understood from his published works; he possessed an extraordinary industry, which was devoted to the acquisition of all possible knowledge, the addition of countless new facts to the fabric of chemistry and mineralogy, and the patient repetition and correction of any observations of others which appeared doubtful. He was singularly unbiassed by any preconceived theory, because he was singularly distrustful of all speculation, and with his industry was combined a remarkable power of accepting new views as soon as they were established, and of relinquishing his old ideas as soon as they were disproved.

His first text-book (1842) is an exposition of the electrochemical theory, and only mentions the new substitution theory of Dumas in order to reject it; but, as a matter of fact, at that date he had himself published a translation of Dumas' lectures on the Philosophy of Chemistry, and a subsequent text-book which he published (1881) is called a "Sketch of Inorganic Chemistry according to the New Views." In the preface he uses the following words: "In the subject of organic chemistry has latterly been introduced a gradual reform of the older views, based upon general principles which underlie the whole science. Those who feel with the author that the modern way of regarding the facts is a real advance, must regret that there is no introductory book available for beginners containing the elements of inorganic chemistry set forth according to the new views. The present outline, without laying claim to any merit, endeavours to supply this need. A supplementary section contains the modern laws, theories, and views so far as they relate to inorganic chemistry."

Rammelsberg was, indeed, one of the first of the chemists brought up in the old school to assimilate the new views and to disseminate them. He published a number of text-books which must have been largely used. His "Grundriss der anorganischen Chemie" ran through five editions; of his "Leitfaden für die quantitative chemische Analyse"

four editions were published; and of his "Leitfaden für die qualitative chemische Analyse" eight editions. In addition to these were published a text-book of chemical metallurgy which ran through two editions; a treatise on theoretical chemistry, one on quantitative metallurgical and mineralogical analysis, and the book already mentioned upon the new views of modern chemistry; it must be remembered that the purpose of all these books was not only to supply the student with a practical handbook, but also to give him an insight into the newer developments of the science.

Combined with his readiness to accept new ideas was an obstinate adherence to the line of work which he marked out for himself, and he never showed the least interest in the development of organic chemistry or took any part in it. His real interest was, I think, in mineral chemistry, of which he was for very many years the most prominent exponent. It is perhaps well that there was one man of untiring industry qualified to receive the torch of mineral chemistry from Berzelius and to keep it alive by his own patient researches during the fifty years when most chemists were attracted by the more dazzling discoveries of organic chemistry.

We will turn now to Rammelsberg's own work. His contributions to science are so numerous that to give an intelligible account of them within a small compass is impossible. They range over the whole domain of inorganic chemistry and mineralogy, and consist mainly of the preparation and analysis of innumerable substances, the measurement and description of innumerable crystals; references to them can be extracted from three of his books "Chemische Abhandlungen," published in 1888; "Handbuch der krystallographisch-physikalischen Chemie," published in 1881—1882; "Handbuch der Mineral-Chemie," published 1875—1895. In the endeavour to convey some impression of the magnitude and thoroughness of his work and of the extent to which the increase of chemical knowledge in the second half of the nineteenth century is indebted to his untiring industry, I shall select a few of his memoirs in chemistry, crystallography, and mineralogy respectively, and let them stand as examples of his labours —a more complete summary being obtainable in the three books which I have just mentioned.

Rammelsberg as Chemist.

In the region of general inorganic chemistry, we can take his investigations upon the halogen compounds, the phosphates, and the cyanides.

Halogen Compounds.—Many of the metallic bromides and iodides had of course been already prepared, and bromic, iodic, and periodic

acids had been discovered, but the knowledge of the iodates and periodates was very limited at the time when Rammelsberg took up their study. He prepared and analysed the bromides of barium, strontium, calcium, magnesium, zinc, cadmium, nickel, cobalt, lead, copper, mercury, and silver ; the bromates of potassium, sodium, ammonium, lithium, barium, strontium, calcium, magnesium, zinc, copper, silver, lead, aluminium, cerium, lanthanum, manganese, iron, nickel, cobalt, cadmium, bismuth, uranium, and mercury.

The bromide of barium was found to contain 2 mols. of water and not 5, as stated by von Hauer ; measurement of the crystals showed them to be isomorphous with the chloride.

But the most important part of the work was the study of the ammonia compounds of the bromides and iodides ; these were prepared either by treating a concentrated solution of the salt with ammonia solution, or by heating the dry salt in a stream of ammonia ; by the former process were prepared $ZnI_2,4NH_3$; $CdI_2,2NH_3$; $CoI_2,4NH_3$; $NiI_2,6NH_3$; $2(CuI_2,4NH_3)+3H_2O$; $ZnBr_2,2NH_3$; $CdBr_2,2NH_3$; $NiBr_2,6NH_3$; $CuBr_2,3NH_3$; by the latter process : $ZnI_2,5NH_3$; $CdI_2,6NH_3$; $CoI_2,5NH_3$; $NiI_2,3NH_3$; $2CuI_2,9NH_3$; $PbI_2,2NH_3$; $2AgI,NH_3$; $2SrBr_2,NH_3$; $CaBr_2,6NH_3$; $CdBr_2,4NH_3$; $CoBr_2,6NH_3$; $NiBr_2,6NH_3$; $CuBr_2,5NH_3$. The composition of all these compounds, their crystalline form where possible, and their behaviour on heating and on treatment with water were studied ; it was shown that ammonia is liberated on heating, and that treatment with water breaks them up into hydroxides and basic salts together with ammonia, and into ammonium bromide or iodide.

The mercury compounds were found to behave differently ; treatment of the solution of mercuric iodide with ammonia solution at the ordinary temperature yields a white, unstable compound, HgI_2+NH_3, identical with that obtained by the dry process, but at a temperature above 60° a brown substance is formed which is stable and is not decomposed by potash ; this has the composition Hg_2INH_2O, and is analogous to the chlorine compound. The now well-known properties of this compound and its behaviour on heating were studied by Rammelsberg, who regarded it as a mercuric ammonium iodide in which 4 atoms of hydrogen are replaced by 2 of mercury.

In 1888, he returned to the study of the ammoniacal mercury compounds, when he determined anew the composition of Millon's base, studied the fusible and infusible varieties of " white precipitate," and by the direct action of acids on Millon's base prepared the mercury-ammonium sulphate, nitrate, carbonate, phosphate, bromate, iodate, and periodate.

The general investigation of bromates, iodates, and periodates belongs to his earlier research ; the bromates were prepared either by

precipitation of metallic salts with potassium bromate or by solution of the oxides or carbonates in bromic acid, and yielded salts of barium, calcium, strontium, lead, mercury, and cadmium crystallising with 1 mol. of water, the copper salt crystallising with 5, and the salts of magnesium, zinc, cerium, lanthanum, nickel, and cobalt crystallising with 6 molecules of water; in addition to these, the bromates of potassium, sodium, ammonium, lithium, silver, aluminium, and mercury were prepared, also basic salts of mercury, bismuth, and uranium, while efforts to obtain the bromates of manganese and chromium were not successful. The isomorphism of the bromates of barium and strontium with the corresponding chlorates was proved by crystalline measurements. In the course of this investigation, Rammelsberg also prepared the ammoniacal bromates of zinc, copper, silver, nickel, and cadmium.

The iodates had only been previously studied by Gay Lussac and Senillas; Rammelsberg was led to their investigation by a desire to test the opinion of Gay Lussac that basic iodates of the alkalis exist. He found that this was not the case, but he proceeded to an exhaustive study of the iodates, in the course of which he prepared and studied the salts of ammonium, potassium, sodium, lithium, thallium, barium, strontium, calcium, magnesium, aluminium, cerium, manganese, iron, cobalt, nickel, zinc, cadmium, lead, tin, bismuth, copper, mercury, and silver, and several of the double salts. This included the crystallographic description of the trimorphous potassium iodate, HKI_2O_6, the double iodate and chloride of potassium, and the double iodate and iodide of sodium; it was shown that sodium iodate crystallises with 1 mol. of water above 5°, and with 5 mols. of water below that temperature; the crystalline form of the latter salt was determined, and it was found that the one substance may be converted into the other by change of temperature.

The ammoniacal iodates of nickel, zinc, and copper were also successfully prepared.

Continuing the research further, Rammelsberg made unsuccessful attempts to prepare perbromic acid and perbromates, and then turned his attention to the periodates. Periodic acid had been discovered in 1833, and a few of the salts had been examined when he took up the subject; he had already shown that among the iodates the potassium salt is the only one which is not converted into a periodate by heating, and in 1838, and again in 1869, he made a special study of the behaviour of the iodates and the periodates at high temperatures; this inquiry included the iodates of potassium, sodium, barium, strontium, calcium, and the periodates of potassium, sodium, lithium, barium, silver, and magnesium. He found that the white, infusible residue which remains after evolution of iodine and oxygen is not a

mixture of oxides, but contains iodine. With considerable difficulty (by determining the volume of the oxygen liberated), it was proved that in the case of the barium salt this is essentially the substance $R''_5I_2O_{12}$, or, as it was then called, fünftel-über-iodsaures Baryum; the existence of these compounds Rammelsberg afterwards confirmed by preparing them in other ways. The result of his laborious study of these compounds, which he made entirely his own, was to supplement, correct, and complete the work of Magnus, Ammermüller, and Langlois, and to establish the whole series of periodates $R'IO_4$; $R'_4I_2O_9$; R'_3IO_5; $R'_8I_2O_{11}$; R'_5IO_6.

The very exhaustive research upon the halogen compounds, of which the above is a very brief sketch, may be taken as an example of Rammelsberg's chemical work. He was not one of those lofty spirits who make a great discovery or are possessed by a great idea which leads them on from one intellectual triumph to another; but he was dominated by a restless zeal for research which made him quick to see the weak points in the investigations of his predecessors, and to mark the missing links in the chain of their researches. This led him at once to take up some piece of work which should either correct or confirm what had gone before, and then his untiring industry tempted him on to make the research as complete as possible.

This seems to me to have been the history of many of his investigations, and is a clue to the scientific character of the man. No difficulty was too great for him, no research was too laborious; having set his hand to the plough there was to be no turning back until the work was finished to his own satisfaction, although from a more modern point of view his limitation of the problem might often appear narrow and his vision of its possibilities circumscribed.

When we take into account that a man imbued with this spirit has worked with unceasing industry for 60 years, we should perhaps scarcely wonder that his discoveries were so numerous and his knowledge so wide. If a complete catalogue were made of the actual facts added to the store of chemical knowledge by Rammelsberg, the result would be amazing by its magnitude.

We must also remember that his independent spirit caused him always to work alone and to master every branch of his research himself. There were few men in Europe between 1840 and 1870 whose practical knowledge of chemistry and crystallography was sufficient to achieve what was accomplished by Rammelsberg.

Phosphates.—It will be sufficient to glance still more briefly at his researches upon the phosphates and the cyanides, and only in such a manner as to illustrate two other features of his character.

Having taken up a problem which was limited in itself, Rammelsberg was often led on by it from one research to another in his desire

to complete the work. This was the case with the particularly difficult work upon the phosphates.

In the course of his mineral analyses he had examined the blue phosphate of iron known as vivianite, which had always been regarded as a ferric phosphate. Rammelsberg discovered that this mineral contained both ferrous and ferric phosphate; his analysis led to the formula

$$2[3Fe_3(PO_4)_2 + 2Fe_2(PO_4)_2] + Fe_2(HO)_6 + 49H_2O,$$

but, since the crystals appear to be isomorphous with the cobalt arsenate, $Co_3(AsO_4)_2 + 8H_2O$, he concluded that vivianite was originally a ferrous phosphate, $Fe_3(PO_4)_2 + 8H_2O$, which by exposure to the air has become partly oxidised to a basic ferric salt. Rammelsberg was never content to express a view without searching patiently for all the evidence which might justify, or if adverse might lead him to modify, his opinion, and accordingly in this instance he proceeded to investigate the oxidation product of artificial ferrous phosphate, and so confirmed his theory. Its truth was still more firmly established some years later by the actual discovery in a sand at Delaware of a *colourless* vivianite which Fisher showed to be a pure ferrous phosphate corresponding exactly to the cobalt arsenate in composition. He also determined the composition of the ferric phosphate prepared from iron-alum and disodium phosphate, and showed how two basic salts can be derived from it.

In the same way, his study of the minerals wagnerite, lazulite, and amblygonite, the last-named a phosphate of aluminium, lithium, sodium, and potassium containing fluorine, which he himself regarded as one of the minerals most difficult to analyse, and whose composition he was the first to determine (1845), led him to work upon the phosphates of magnesium and aluminium. He proved the gelatinous precipitate yielded by concentrated solutions of magnesium sulphate and disodium phosphate, after washing in the cold, to have the composition $HMgPO_4 + 3H_2O$, while the filtrate yielded Graham's crystallised hydrate, $HMgPO_4 + 7H_2O$; by treatment with boiling water, the normal salt, $Mg_3(PO_4)_2 + 5H_2O$, is obtained. A study of the gelatinous precipitate obtained by mixing solutions of alum and disodium phosphate led him to the conclusion that the substance $Al_2(PO_4)_2$ may contain either 9 or 6 mols. of water.

The lithium phosphates, both mineral and artificial, were the subject of repeated research on his part; none had been quantitatively analysed with the exception of the sodium lithium salt; Rammelsberg proved the existence of the three salts $Li_3PO_4 + aq$, H_2LiPO_4, $H_5Li(PO_4)_2 + aq$. He further investigated the double salt of di- and tri-lithium phosphate, the sodium lithium phosphate, and the

lithium pyrophosphate; showed the precipitate obtained from one molecule of $Na_4P_2O_7$ and six molecules of lithium acetate to be an isomorphous mixture containing varying proportions of sodium and lithium, and found that the acid pyrophosphate, $H_2Li_2P_2O_7$, could not be obtained in a pure condition.

His investigations on the phosphites were undertaken with the object of ascertaining the basicity of the acid. H. Rose had studied the behaviour of the phosphites on heating, and (like Berzelius) had found them to have the composition $2RO,P_2O_3$, but to contain various proportions of water, the barium, strontium, and calcium salts having 2 mols., and the lead and manganese salts only 1 mol. of water of constitution, so that they were to be referred to the two acids $R_2H_4P_2O_7$ and $RHPO_3$. Wurtz, on the other hand, regarded them all as neutral salts containing 1 mol. of water. The controversy turned mainly on the composition of the phosphite of barium which Rose had found to be $H_4Ba_2P_2O_7$, while Wurtz regarded it as $HBaPO_3$. Rammelsberg repeated the analyses, and found the lead salt to be $HPbPO_3$ and the barium salt to be $H_4Ba_2P_2O_7$, thus confirming the results of Rose and Berzelius.

Having found that oxidation of barium phosphite with nitric acid yielded a mixture of oxide, metaphosphate, and pyrophosphate, he was led to investigate anew the phosphites of strontium, calcium, magnesium, zinc, manganese, nickel, cobalt, cadmium, lead, copper, and iron, especially as regards their behaviour on heating. As the result of these investigations, he concluded that there are three phosphorous acids, H_3PO_3, $H_8P_2O_7$, and H_5PO_4, derived from the union of $H_4P_2O_5$ with 1, 2, and 3 molecules of water respectively; to the first class belong the salts of potassium, sodium, ammonium, magnesium, zinc, cobalt, manganese, cadmium, lead, and copper; to the second, the salts of barium, strontium, calcium, magnesium, nickel, and zinc; and to the third the salt H_3MgPO_4. When Prinzhorn and Precht, in 1875, showed that the barium phosphite contained a certain proportion of phosphate, to which the inconsistencies were due, Rammelsberg at once gave up all these views and convinced himself that the salt really has the composition $HBaPO_3$, and that Wurtz was, after all, in the right.

He subsequently undertook the study of the hypophosphites with the view of supplementing the work of H. Rose and Wurtz, and of preparing as many of these interesting compounds as possible, especially for the purpose of a crystallographic investigation. He prepared and studied the hypophosphites of ammonium, sodium, thallium, lithium, barium, strontium, calcium, magnesium, zinc, manganese, cerium, cadmium, lead, cobalt, nickel, and uranium, and compared their isomorphous relationships where they exist.

When it is remembered that in this and many similar pieces of work Rammelsberg spared no pains in preparing, not only material for analysis, but also crystals which could be crystallographically studied with all the means at his command, and that the whole work of measurement and calculation was done by himself, one may well be surprised that even in his long life of activity so many of these researches were carried out.

Cyanides.—If our knowledge of the halogen compounds and of the phosphates, phosphites, and hypophosphites is largely derived from the labours of Rammelsberg, still more is this the case with the double cyanides. His work upon these began with his inaugural dissertation in 1837, of which the purpose was to complete the work of Gmelin, Wöhler, and Ittner by the preparation of the potassium and cadmium double cyanides.

It is scarcely necessary to recapitulate the long series of compounds which he prepared; they have become a part of the edifice of inorganic chemistry, throughout the whole framework of which the handiwork of Rammelsberg is to be traced by those who care to look up the authorities for the accepted facts of the science.

A large portion of the work was devoted to the behaviour of cyanides and double cyanides at higher temperatures, to which he was led by Thaulow's discovery of paracyanogen and his work upon the decomposition of cyanide of silver by heat. He repeated these experiments and found that the so-called carbazote, obtained by heating cyanide of silver, differed in no respect from cyanogen; his further experiments upon the double cyanides were chiefly devoted to the determination of the nature of the distillation residues obtained on heating.

Upon the subject of the double cyanides, Rammelsberg held very decided views, and expressed himself as strongly opposed to the ferrocyanogen theory of Porret and Liebig. His position is perhaps best stated in his own words, which will serve to illustrate the clear and direct character of his statements, and also, perhaps, the prejudices by which his views were limited:

"According to the ferrocyanide theory, Prussian blue is not $3FeCy_2 + 2Fe_2Cy_6$, but $Fe_4,3FeCy_6$. Gmelin's blue is not $3FeCy_2 + Fe_2Cy_6$, but Fe_3,Fe_2Cy_{12}."

(Rammelsberg always in his teaching preferred to use the name "Gmelin's blue" in place of "Turnbull's blue.")

"Now, as is well known, there are two other compounds, namely:

"(1) $KCy + FeCy_2$, which is separated when yellow prussiate of potash is heated with dilute sulphuric acid. According to the ferrocyanide theory, it would be treated as $K_4,FeCy_6 + Fe_2,FeCy_6$.

"(2) $KCy+2FeCy_2$, the red precipitate obtained from potassium cyanide and ferrous salts, which was investigated by Städeler. If it is treated as K,Fe_2Cy_5, a third radicle must be assumed. The adherents of the ferrocyanide theory maintain that all double cyanides fall into two classes:

"A. Simple haloid salts of a substance consisting of cyanogen and a metal. To this class belong the series $4KCy+RCy_2$, and the series $6KCy+R_2Cy_6$, and also from the series $2KCy+RCy_2$, the platinum and palladium compounds. In these the following radicles must be assumed:

$$RCy_4\,;\ RCy_6\,;\ R_2Cy_{12}.$$

"B. Double salts. This includes the remainder of the series, $2KCy+RCy_2$, and also the salts of gold, silver, and copper.

"But why should this difference of constitution be assumed?

"The salts of the first class (we refer in particular to the potassium compound) yield in solution with dilute acids at ordinary temperatures no prussic acid, as do those of the second class.

"The reason why the former apparently suffer no decomposition is to be found in the formation of a corresponding hydrogen compound.

"This action of acids, however, is limited to a portion of the salts. Whilst yellow and red prussiate obey the rule, and potassium cobalt cyanide behaves in the same way, my experiments show that the solution of potassium manganese cyanide, which decomposes of itself with liberation of manganese oxide, yields prussic acid freely with acids, and the same is true of potassium chromium cyanide. The hydrogen compounds prepared from the corresponding salts liberate hydrogen cyanide freely when their solutions are heated. The ferrocyanide theory assumes that here $H_4,FeCy_6$ is converted into $4HCy$ and $FeCy_2$.

"The potassium salts of ruthenium and osmium are also decomposed by acids with formation of the hydrogen compounds, whose solutions quickly liberate prussic acid and deposit $RuCy_2$ and $OsCy_2$.

"How different may be the behaviour of analogous and isomorphous salts towards acids is illustrated by $K_6Ir_2Cy_{12}$, which behaves like the red prussiate, while $K_6Rh_2Cy_{12}$ yields prussic acid and Rh_2Cy_6.

"Hence the action of the cyanogen compounds with acids is not a sufficient reason for assuming two classes of different constitution. Their liability to decomposition varies greatly, and is weakest in the iron compounds.

"Closely related to the behaviour of the double cyanides towards acids is their physiological action. But to adduce this action, which is limited to the experiment with potassium iron cyanide, in support of the ferrocyanide theory is wholly unjustifiable, for the physiological action of a chemical compound does not depend upon the nature and association of its elements.

"If now the behaviour of the double cyanides towards acids is not such that it implies a difference in their constitution, but only indicates a more or less intimate union of the two components, which, in the compounds of zinc, cadmium, copper, &c., is admittedly so weak that the precipitates yielded by the potassium salt with other metallic salts are either of a different composition or merely mixtures, then the only support for the hypothesis of a ferrocyanide and other metallic radicles falls to the ground.

"The behaviour of the double cyanides towards hydrogen sulphide or alkaline sulphides, the impossibility of precipitating the iron as sulphide from

prussiate of potash, which is adduced by some as a further support of the ferrocyanide theory, is based upon an almost incredible ignorance of the facts.

"It has long been known that potassium cyanide dissolves many of the metallic sulphides with production of potassium sulphide, $6KCy + FeS = 4KCy + FeCy_2 + K_2S$. It is therefore self evident that alkaline sulphides cannot precipitate sulphide of iron from prussiate of potash."

It is easy now to see how Rammelsberg failed to appreciate modern distinctions between double salts and salts of complex acids. I think that even his later papers take no account of contemporary work upon electrolytic dissociation. Neither did he pay any attention to the important aid afforded by the complex cyanides in the periodic classification of the metals, especially the Fe, Co, Ni, and Pt group. And similarly in the halogen compounds there is no evidence that he would have attached much importance to the use made of the salts of silver bromide with ammonia in developing the theory of dissociation by Joannis and Crozier and others. But, perhaps, this is unfair anticipation, for his own researches belong to a much earlier period.

Among the other large contributions to general inorganic chemistry must be mentioned Rammelsberg's researches upon the sulphantimonates; he was the first to determine the composition of Schlippe's salt, and to prepare and study a great number of these compounds, and the potassium antimonyl sulphantimonate was of special interest 60 years ago as the first instance of a double salt whose constituents have the same electropositive element; he also undertook a laborious repetition of Rose's work upon tantalum and niobium, which had been called in question and partly disproved by Marignac and Blomstrand, so that a complete revision was necessary in order to confirm what was right and to eliminate what was wrong. In Rammelsberg's own words: "It seems an irony of fate that H. Rose, the discoverer of the volatile oxychloride of chromium, who proved that the supposed superchlorides of molybdenum and tungsten are oxychlorides, should himself have taken niobic oxychloride for niobic chloride (Unterniobchlorid). Similarly, as is well known, Berzelius took the vanadium oxychloride for vanadium chloride, as was first proved by Roscoe. Of Rose's results, all that relates to his Unterniobsäure is correct, but his niobium compounds were mixtures, and his tantalum compounds were not free from niobium. Rose's memoirs are to be found in Poggendorff's *Annalen*, volumes 63—113. I have extracted from them all that is firmly established both now and for the future of the science (*ibid.*, 136, 177)." Mention only can be made of Rammelsberg's researches upon ozone, upon the hyposulphites, the sulphites, nitrosulphonic acid, the nitrites, titanic acid, the vanadates, the phosphomolybdates, the salts of uranium, of thallium, of cerium, and of lithium, and his determination of the atomic weights of

molybdenum, cerium, lanthanum, uranium, and of the metals of the yttrium group. In the last-mentioned he strongly opposed the view of Nordenskiöld that the atomic weight of these metals is nearly constant in the minerals which contain them.

One of his important papers was communicated to this Society, "Experimental Researches on the Amalgamation of Silver Ores" (Trans., 1881, 39, 374). Being engaged upon a translation of Percy's metallurgy into German, he was struck by the very imperfect experiments which had been made with the object of discovering the chemical changes which take place in the Mexican amalgamation or Patio process. With characteristic energy he made it his first business to repeat and extend these experiments, and to obtain for the first time quantitative results. He studied the action of cuprous and cupric chlorides on silver chloride, sulphide, arsenide, sulpharsenide, and sulphantimonide, and although it cannot be said that his experiments dispelled the mystery that surrounds the Mexican process, they supplied for the first time numerical data on which the explanation of that process must be based.

One of the most unintelligible features of Rammelsberg's scientific work has been alluded to above, and must be again noticed. During the period when the whole science of chemistry was being transformed by its development on the organic side, Rammelsberg, almost alone, remained steadfastly immersed in inorganic research, and was never tempted into the attractive region of the carbon compounds. With the exception of a few isolated researches, mostly of a crystallographic nature, his work upon the oxalic acids and their salts and upon the uranium acetates are the only important investigations which carried him across the borderland, and these are almost entirely of crystallo-chemical interest.

It was not that he closed his eyes to the extraordinary development of organic chemistry, or failed to make use of its teaching ; indeed the subject is adequately treated in his own text-books, and, as I have pointed out, he was one of the earliest adherents of the new chemistry ; but he purposely confined himself to a path which he had marked out at the beginning of his career, except where his own researches led him to make temporary excursions into the region of allied subjects.

Rammelsberg as Crystallographer.

In 1801 Haüy had written that "at the École des Mines, chemistry and crystallography, so long separated, had entered into a close partnership which they have promised never to dissolve." No one contributed more to the maintenance of this partnership than Rammelsberg.

Of his own work on the acetates, he says : "The previous data con-

tained so many contradictions that, evidently, the material which was analysed and the material which was measured cannot always have been the same. A work carried out along both lines has removed all the doubt and error which resulted from the fact that the chemist did not measure the salts which he analysed, and the crystallographer did not analyse the salts which he measured."

For example, he showed in this paper that two manganese uranyl acetates crystallise out in succession from a mixed solution of the acetates, and that the measurements of Grailich had been made upon one of these, and the analysis of Weselsky upon the other; they had, of course, been supposed to relate to the same substance.

It is painful to reflect how often this sort of thing may have happened during the nineteenth century, and the reproach against chemists that they lack a practical knowledge of crystallography, and against crystallographers that they lack a practical knowledge of chemistry, is by no means removed. It is, however, a hopeful sign of the times that a younger school of chemists is now rising against whom this reproach can no longer be brought.

Even in 1881 Rammelsberg could use the following words on the subject ("Handbuch der krystallographisch-physikalischen Chemie," preface):

"Physicists and chemists meet in a region which stimulates the research spirit of both. Has not specific heat acquired a great importance for chemistry? Has not the electrolysis of compounds exercised an effect upon the views of pure chemistry? Have not spectroscopic phenomena been transferred from the domain of optics to that of practical chemistry? The chemist sees himself continually driven to the study of physical phenomena. . . . The chemist must investigate the geometrical and other physical properties of substances as well as their composition and reactions. . . . If, however, we compare our chemical handbooks with the mineralogical, we cannot fail to notice the very unequal treatment which the individual properties receive. For each mineral is given a special description of the crystalline form; *i.e.*, the constants obtained by observation and calculation. . . . The handbooks of chemistry, even the more complete, treat the most important physical properties either in a fragmentary manner or not at all. This is true of the crystalline form, the optical characters, the expansion, specific heat, electrical and magnetic properties; the reader is left to seek the physical constants of a substance in physical treatises or journals. Leopold Gmelin's great work alone takes due account of the crystallographic elements.

"A result of this neglect of the physical properties in our chemical textbooks is the incompetence of young chemists to investigate their own preparations crystallographically and optically. And yet it is not so difficult to acquire the requisite crystallographic and physical knowledge, instead of leaving this investigation to others. In a precisely opposite manner the mineralogists formerly erred by confining themselves to the geometrical and physical properties, and neglecting the chemical, so that we learnt from them what a

mineral looks like but not what it is. A substance bearing the same name, but analysed by another man in another place and at another time, was often an entirely different mineral. Such a division of labour frequently leads to blunders ; an instructive example is afforded by the memoir of Schabus, which was crowned by the Vienna Academy of Sciences (in 1855). In this, potassium lithium sulphate is described as lithium sulphate, the sulphates of didymium and lanthanum are described as the chlorides, under the name grape-sugar is described the compound with sodium chloride, &c."

One of Rammelsberg's great books of reference, from the preface of which the above is quoted, was designed to supply the need of which he complains, and to give chemists a book in which they could find precisely what was wanting in their own treatises. With immense labour he collected for this book all the crystallographic, optical, and other physical constants of all the crystallised compounds which had been described, adding full references so that the reader could always turn to the original sources. It was, and is still, an invaluable book of reference, although, of course, the volume dealing with organic compounds is now quite inadequate, owing to the rapid accumulation of facts during the last 20 years; it would no longer be possible to include all the physical as well as the crystallographic characters of chemical compounds in a single volume of reasonable dimensions ; and the modern method of treating the former in separate works is, no doubt, more convenient.

To the crystallographic knowledge of chemical compounds no man contributed more largely than Rammelsberg himself. Without his labours, the illuminating discovery of isomorphism would never have exerted such widespread influence, and no man was better fitted to carry on the work of his great master, Mitscherlich.

In crystallography as a distinct science, Rammelsberg had, I think, no particular interest ; he regarded it only as a means to an end. Born only four years after the discovery of the reflecting goniometer by Wollaston, he became one of the most practised experts with that instrument, and regarded it as part of the armoury of the chemist.

His student days were set at an interesting time in the history of the young University of Berlin. The Abbé Haüy, the real founder of crystallography, was still alive, and the science had made rapid advances in the hands of German and English investigators. Weiss had recently introduced the use of axes to which the faces of a crystal can be referred and which suffice for its description ; he and Mohs had independently established the existence of the six systems ; the laws of the double refraction of crystals belonging to these different systems and the methods by which they can be studied had been elaborated by Brewster and Herschel. In no place could the newly

developed science be better studied than in Berlin; Mitscherlich was Professor of chemistry, Weiss of mineralogy, and Gustav Rose had recently (1822) been appointed ausserordentlicher Professor of mineralogy.

Rammelsberg worked with all these men, and his whole scientific career was determined by their inspiration, but he always remained content with the crystallographic methods of his student days, and was satisfied if he could determine the form of every crystallised compound which he prepared and express it in the manner which had become familiar to him in 1834. Weiss called the three axes of a crystal *a b c*, and denoted any face by its intercepts on these axes by means of a symbol such as [*ma*, *nb*, *pc*]. Rammelsberg always employed this notation; Neumann in 1823 had already introduced the convenient method of denoting the faces of a crystal by their normals and by the points in which they intersect a sphere, and Whewell in the same year had suggested the use of indices, afterwards developed by Miller, according to which a face whose intercepts on the axes are $\frac{a}{3}, \frac{b}{2}, \frac{c}{4}$ is denoted by the symbol (324); yet he would not even adopt the notation of Naumann, which became almost universal in Germany. He says in 1881 "I have used the notation introduced by Weiss, the founder of the new crystallography, because I regard it as in itself better than any other, and I employ the actual angles between the faces because they alone, and not the angles between the normals, are expressed by the crystal itself. It is certain that the study of crystals would have been much more widely diffused among chemists if crystallographers had followed neither Naumann nor Whewell and Miller."

This was a curious piece of conservatism which would hardly have been expected on the part of one who, as we have seen, was so quick to absorb new views in chemistry and to change his position in conformity with the advance of that science. Having regard to the rapid displacement of Weiss's system by Naumann's, and the present almost universal acceptance of Miller's notation, it is easy to see that this adherence to an antiquated notation was one of the chief causes which prevented his book from becoming more widely known. For this reason, also, it is probable that two elementary text-books of crystallography for chemists, which he published in 1857 and 1883 respectively, never had a wide circulation, although they are written with admirable lucidity.

None the less is the Handbook an invaluable storehouse of useful information, and none the less were Rammelsberg's own contributions to chemical crystallography of immense importance. Let us, without entering into details, glance at a few of his investigations. Among

those of most general interest are his work upon the isomorphism of sulphur and selenium, and of the compounds of vanadium and phosphorus.

From experiments on the density and the solubility of selenium, Rammelsberg concluded that there are three, and not two, crystalline modifications of this element, in addition to the amorphous variety. Mitscherlich had measured crystallised selenium with great care, but found its form to be different from that of sulphur; Rammelsberg showed that the crystals obtained from solution in carbon disulphide are probably isomorphous with the monoclinic variety of sulphur, and this conclusion was afterwards confirmed by vom Rath, who found that isomorphous mixtures of the two elements possess sometimes the form of orthorhombic, but sometimes the form of monoclinic sulphur, proving that a monoclinic modification does enter into such mixtures. He subsequently endeavoured to prepare the potassium tellurate which had been described as isomorphous with the selenate and sulphate, but found no justification for the suggested isomorphism of tellurates with selenates. The isomorphism of sulphur and selenium has since been the subject of research by Muthmann, who has established the crystallographic relationships between these elements so far as they are at present known, and he is not disposed to accept the isomorphism of the selenium crystals here alluded to with the ordinary monoclinic sulphur, although it may occur with another monoclinic modification.

In 1856 Rammelsberg pointed out that the mineral vanadinite, the chlorovanadate of lead, in which vanadium was first discovered, is undoubtedly isomorphous with pyromorphite, the chlorophosphate, and insisted that the isomorphism must imply an analogous formula, especially since vanadinite contains some phosphoric acid, as he found by the analysis of specimens from Carinthia. At that date, the views that were held concerning the constitution of vanadic acid did not render this interpretation possible, and Rammelsberg declared that this must either be a case of the isomorphism of substances which are not similar in constitution, or else vanadic acid is not VO_3, but V_2O_5, hereby predicting the result of Roscoe's classic work.

From what has been already said, it will be understood that, among the bromides, bromates, iodides, iodates, and periodates, the phosphates, phosphites, &c., and the cyanides, the isomorphous relationships of many series of salts were established by Rammelsberg; the same is true of the double chlorides, such as $2R'Cl + R''Cl_2 + aq$; the dithionates; the arsenates, &c.

Among the phosphates, he showed that H, K, Am, Tl replace one another in isomorphous salts. Among the uranyl double acetates he traced three series in one of which manganese is replaced by cadmium, and in another by magnesium, whilst in the third magnesium is replaced by zinc, nickel, cobalt, or iron; the barium, strontium, and calcium

series, containing 2 atoms of uranium and 6 mols. of water, constitute another isomorphous series, whilst in the alkali series potassium may be replaced by silver. Among the sulphates, he contributed cases of the isomorphism of yttrium, erbium, didymium, and cadmium, and of uranium with thorium.

Many of these researches bore upon the isomorphism of compounds containing the alkali metals. He was the first to establish (in 1853) the tetartohedral character of sodium chlorate by observing that a cube of this substance might have only four faces evenly replacing its corners and twelve faces unevenly replacing its edges; he was also the first to make crystalline mixtures of cubic sodium chlorate with tetragonal silver chlorate; his preparations were afterwards used by Lehmann and served to demonstrate the fact that silver chlorate is dimorphous. He established also the dimorphism of manganese chloride, and proved the isomorphism of tin, platinum and palladium in the double chlorides. The polymorphism of tin itself was the subject of a special investigation in which he studied in particular the transformation of ordinary into gray tin and came to the conclusion that there are three modifications of this element, and that gray tin may become transformed below its temperature of fusion into tetragonal and perhaps also into ordinary tin; in this connection, the alterations which take place in the alloy used in organ pipes after continued use, possibly due to vibration, are of interest. He measured crystals of an alloy of tin and copper which proved to be hexagonal, and adduced strong reasons for regarding many other alloys such as those of copper and zinc, gold and tin, iron and tin, tin and antimony, gold and antimony, gold and mercury, as mixtures of isodimorphous substances.

His early experiments on the solubility of mixed sulphates (in 1854) were the first observations of this sort, and were the beginning of a class of research which has subsequently, in the hands of Bakhuis Roozeboom and others, led to such fruitful results. In these and kindred researches, Rammelsberg may be regarded as one of the pioneers of modern physical chemistry. He was the first to suggest a principle which has since been elaborated by Wyrouboff and others, that the axial ratios of the substances which are capable of forming mixed crystals are not necessarily almost identical, but may bear a simple rational relation to each other; the possibility of isomorphous substances presenting almost identical angles in some zones of crystal faces whilst differing considerably in others is brought out in his study of the phosphates of ammonium, thallium, and sodium.

The most interesting of his memoirs on these subjects, and, considering the date at which it was published (1854), the most remarkable, was that already referred to upon mixed crystals of the sulphates of the series $R''SO_4,7H_2O$. He found that the crystals obtained by

fractional crystallisation do not possess the same composition as the solution from which they crystallise, if the solubility of the constituent salts is not the same, but that successive crops are produced of which the last contain a greater proportion of the more soluble salt; he also showed that in some of these cases the mixed crystals are only capable of forming within certain limits, and that an excess of one constituent may crystallise out in a pure condition beside the crystals of mixed constitution; further, that in such mixtures, for example, as those containing iron and magnesium, the crystals possess the rhombic form of magnesium sulphate when Mg : Fe is greater than 3, and the monoclinic form of the ferrous sulphate when Mg : Fe is equal to or less than 1.

At that date, such mixed crystals were usually supposed to be mere parallel growths consisting of alternate layers of the two constituents; Rammelsberg made it very clear that their complete homogeneity and their optical properties proved them to be really molecular mixtures. In this very important work, he was opening up a line of research which leads directly to all that has since been done upon the properties of solid solutions, and induces me to repeat that Rammelsberg, although he has not received the credit for it, was certainly one of the pioneers in modern physical chemistry.

It is not necessary to pursue this subject further; it is now familiar to all chemists, and an admirable summary of the subsequent work is to be found in the English translation of Fock's "Introduction to Chemical Crystallography."

One striking result of Rammelsberg's work on the mixed sulphates deserves notice; his analyses of the mixed sulphates led him to the conclusion that, in some of these at any rate, the mixture does not take place in arbitrary proportions, but only in certain fixed molecular proportions; in other words, that they are of the nature of double salts, although their properties may be indistinguishable from those of a mixture. Since the publication of Dufet's research, which indicated a continuous change of the geometrical and physical properties as the composition of the mixed zinc–magnesium sulphate changes, this result has been ignored; but Rammelsberg was a careful observer, and his experiments ought to be repeated.

I have perhaps now quoted enough of his crystallographic work to show what valuable results he was able to obtain by his familiarity with the use of the goniometer, and his recognition of the fact that this instrument should form part of the equipment of a chemist.

Of the all important work relating to isomorphism that formed so large a part of Rammelsberg's labours, the greater portion lies in the field of mineralogy, where his contributions to science were even more

extensive than the chemical and crystallographic researches which we have just surveyed.

Rammelsberg as Mineralogist.

In attempting now to form an estimate of Rammelsberg's labours, which have long become a part of the scientific heritage of the present generation, we must continually bear in mind that, although he died in 1899, he was beginning to publish in 1837, and it is necessary to picture to ourselves the condition of science at that date. This is true of his chemical and crystallographic work, and it is equally true of his mineralogical memoirs in which both chemistry and crystallography are combined. Fortunately, it is easy to get a picture of the condition of mineralogy at different periods in his career, for the standard text-book was the work of his exact contemporary, Professor James Dwight Dana, and the successive editions of that book reflect accurately the successive stages of the science. The first edition was issued in 1837, the very year in which Rammelsberg's first work was published; the sixth edition, edited by Professor Edward Dana, was issued in 1892, when Rammelsberg had just resigned his professorship; the immense difference between the two in their chemical aspect is really an eloquent testimony to the influence of his work.

In 1837, mineral chemistry did not exist except in the mind of Berzelius, and perhaps of one or two of his followers. In the first edition of Dana's mineralogy, not a single formula is given, and in the preface the following remarkable statement occurs: "When the crystallisation of a species is sufficiently distinct to serve as a guide in distinguishing species, the results obtained by chemical means should never modify the decisions of the mineralogist," and, subsequently, after it has been confessed that chemical and blowpipe tests are often a valuable assistance, "in making this admission it does not appear that we degrade the science of mineralogy from its rank among the natural sciences as some of its most distinguished authors would affirm."

That a mineralogist should have to apologise for analysing a mineral, and regard an analysis as a degradation to his science, seems now scarcely credible, but so it was in 1837. It is true that some glimmering of the influence of Berzelius may be discerned in the shape of a little appendix on chemical classification. Minerals, it is there said, may be classified either by their electropositive or by their electronegative elements; the latter is perhaps preferable, for Mitscherlich's principle of isomorphism has shown that the electropositive elements may replace each other without introducing any change into the physical characters. On the other hand, later discoveries indicate

that the electronegative constituents may also replace each other; so that on the whole there is an objection to any chemical classification whatever.

The second edition appeared in 1844. Here the classification adopted is that of Mohs—the latest refinement of the so-called natural-historical system of Werner—in which the species are defined by their external characters alone, especially the hardness and the specific gravity, and not by their composition. The species are grouped into genera, and the genera into orders, and they all receive Latin names like those used for plants.

In this second edition, however, the appendix on chemical classification contains a survey of the mineral kingdom in which the species are arranged solely by their chemical constitution, and are defined by chemical formulæ. The secret of this change is explained by the author himself; he says, "The very elaborate treatise on chemical mineralogy by Rammelsberg, which has lately appeared in Germany, has afforded nearly all the materials for this part of the table."

It will be found that at this date, over seven years after he had began to publish, Rammelsberg is already responsible for no less than 56 of the formulæ, and in succeeding editions his influence is no less strongly felt. In the third edition of Dana, the natural history system is thrown over, and the classification becomes mainly a chemical one, and nearly identical with that adopted at the present day.

This transformation of mineralogy was, of course, originally due to Berzelius; its beginnings are sketched in Whewell's "History of the Inductive Sciences," where it is treated as an almost contemporary episode.

Berzelius had first, in 1816, proposed a classification of minerals according to the electropositive elements, and subsequently, when this had been subjected to much criticism and was found to be incompatible with various isomorphous relationships, he replaced it by an arrangement mainly according to the electronegative elements.

No one interested himself more in the dissemination of the views of Berzelius than his friend Rammelsberg, who published in 1847 a small volume containing translations by Gmelin, Pfaff, and himself of seven memoirs by Berzelius relating to the classification of minerals. Two of these are the schemes just referred to, the others are replies to his various critics, and the volume closes with a paper by Rammelsberg himself, a survey of the mineral kingdom upon the lines laid down by Berzelius.

In a preface, he remarks "According to this principle the different augites, hornblendes, garnets, &c., which contain different bases cannot be placed together. But whatever may be the objections to

the chemical system from the purely mineralogical standpoint, it cannot be denied that it is based upon a single principle, and that this can be conveniently carried out through the whole scheme."

It was, I think, characteristic of the man that he did not devote any more time to the academic discussion of the principles of classification —in his own first treatise the minerals were arranged by the most convenient of all methods, an alphabetical order—but, having convinced himself that a chemical system would be possible, he set to work upon the analyses without which any such classification would be premature.

The treatise was entitled "Handwörterbuch des chemischen Theils der Mineralogie," and was published in 1841; it was dedicated to Heinrich and Gustav Rose. The book contains all the mineral analyses at that time published, including a number of new analyses by Rammelsberg himself, and gives the reactions and blowpipe tests for each species. All the formulæ are calculated from the atomic weights of Berzelius, and the theoretical composition of each mineral is given. A few pages of introduction give the principles of mineral chemistry as laid down by Berzelius, and the method of calculating formulæ.

The book was welcomed with acclamation by Berzelius, Leonhard, Kobell, and the other leaders of chemical and mineralogical science. In his Jahresbericht for 1843, Berzelius gives the following appreciation of the work:

"Mineralogy has been enriched by a work of the highest value to those who believe that the study of the chemical composition of minerals belongs to this science. The minerals are arranged in alphabetical order and all their known analyses are given, accompanied by a profound criticism of the analytical methods employed therein, together, often, with a recalculation and the requisite correction of the results deduced. It fulfils two requirements which are seldom simultaneously satisfied, it is exhaustive without being wearisome by excessive elaboration. The introduction contains a brief but clear and systematic representation of the chemical constitution of minerals, and the way in which they are to be criticised according to the results of the analyses.

"Seldom has a book been so much needed or so well supplied the need. The industrious author deserves the greatest thanks for his useful and laborious undertaking."

Between the years 1843 and 1853, five successive supplements were issued at intervals; not only did these contain all the new analyses which had been published, but the composition and formulæ were all recalculated with the corrected atomic weights.

It will by this time be suspected from what has gone before that most of Rammelsberg's life was devoted to the laborious accumulation of new facts, and that he did not publish much of a speculative nature or enter into the wordy strife of scientific controversy; he was content

to criticise and correct by the quiet process of experiment and observation.

Each of these supplements to the Handwörterbuch contains a general introduction which gives a clue to what he considered most important and interesting in contemporary mineralogy and to his own opinions on controversial subjects.

For instance, in the second supplement (1845), he explains that Gmelin had accepted SiO_2, in place of SiO_3, as the constitution of silica. The formulæ of most of the important silicates on this hypothesis are given, and Rammelsberg confesses that many are considerably simplified, but the principle is not yet accepted.

The third supplement (1847) contains a notice of Wallmark's suggestions concerning silicates of the monoxide bases, namely, that in these, whatever may be their differences of system, two of the crystallographic axes bear nearly a constant ratio 0·92 : 1. The recent investigations which led to the detection of phosphoric acid and fluorine in very many minerals, and Ebelmen's work on the decomposition of silicates, are also noticed.

In the fourth supplement (1849), the recently suggested possibility of the isomorphism of sulphur and arsenic compounds is discussed, and Rammelsberg thinks it cannot be maintained.

The relationship between the rhombic bournonite ($PbCuSbS_3$) and the hexagonal red silver (Ag_3SbS_3), which had been compared by Gustav Rose to that between aragonite and calcite, is in his opinion due to proportionality of atomic volumes.

$$\frac{\text{Calcite}}{\text{Red Silver}} = \frac{232}{1180} = \frac{1}{5}\ ;\ \frac{\text{Aragonite}}{\text{Bournonite}} = \frac{214}{1073} = \frac{1}{5}.$$

The greater part of these introductions, however, is devoted to a criticism of Scheerer's polymeric isomorphism and of Hermann's heteromerism ; it is difficult now to appreciate the importance which these theories assumed in the eyes of their contemporaries, and it is almost forgotten how large a part was played by Rammelsberg in their demolition. In Ernst von Meyer's "History of Chemistry," Rammelsberg is dismissed in a paragraph (he is also killed before his time), and the Hermann—Scheerer controversy is scarcely discussed ; and yet these views must have, for a time, held the field masterfully. In his fourth supplement, Rammelsberg prefaces his criticism with the remark "The criticism of Scheerer's and Hermann's theories may, it is hoped, induce others to express their opinions openly." Scheerer, it will be remembered, believed that in many silicates and other minerals RO may be replaced by $3H_2O$; his argument relied chiefly upon the mineral aspasiolite, which has the form of cordierite, and also a similar composition if 1 mol. of magnesium oxide may be regarded as replaced by

3 mols. of water. The serpentine crystals from Snarum in Norway were supposed to be another example. Rammelsberg insisted that aspasiolite and the allied minerals are only altered cordierite which has gained water during decomposition (the mineral has subsequently, owing to the work of Haidinger, Naumann, and others, been deposed from its high position, and is now known to be certainly a pseudomorph after cordierite); Rammelsberg also showed that the minerals of the scapolite group upon which also Scheerer largely relied are particularly liable to alteration. The arsenate of cobalt, according to Scheerer, contains 6 mols. of water, and its isomorphism with the ferric phosphate, vivianite, is only brought out by assuming that FeO is replaced by $3H_2O$; Rammelsberg insists that both minerals contain 8 mols. of water. Scheerer's further hypothesis that CuO can be replaced by $2H_2O$, and $2SiO_2$ by $3Al_2O_3$, he stigmatises as entirely arbitrary.

Hermann's heteromerism, which has also passed into the limbo of forsaken theories, and is dismissed by Arzruni in his volume on the physical chemistry of crystals in Graham-Otto's Lehrbuch as of no importance, was criticised by Rammelsberg with great care, and I think will be found on examination to be far less alien to modern views than is commonly supposed. The real hypothesis of Hermann was that substances of nearly the same form, but quite different composition, can mix to form homogeneous crystals ; epidote, for example, is a mixture of the two following compounds :—

Zoisite..... $\dot{R}_2\dddot{S}i + 2\dddot{R}\dddot{S}i$

Bucklandite ..... $2\dot{R}_2\dddot{S}i + 3\dddot{R}\dddot{S}i$.

That substances of different composition may have nearly the same form Rammelsberg confesses ; that they can enter into isomorphous mixtures he regards as not proven, but contents himself with the principle. "Substances which have nearly the same crystalline form possess the same or proportional atomic volumes."

The fifth supplement (1853) gives evidence of the rapidly extending acceptance (due largely to Dana and Kobell) of Kopp's idea that the isomorphism of minerals depends upon the equality or proportionality of their atomic volumes. Rammelsberg himself at that date regards

Tourmaline as $\dot{R}_3\dddot{S}i_2 + n\dddot{R}\dddot{S}i$ with $\dot{R}\dddot{S}i + n\dddot{R}\dddot{S}i$.

Felspar as $\dot{R}_n\dddot{S}i + n\dddot{A}i\dddot{S}i_n$.

Mica as $n\dot{R}\dddot{S}i + n\dddot{R}\dddot{S}i$.

Hornblende as $n\dot{R}\dddot{S}i + n\dot{R}_3\dddot{S}i_2$.

These are all instances of the multiplying cases of isomorphism among compounds which differ in the number of their atoms.

From that day to the present time, mineral chemistry has been mainly occupied with the endeavour to discover the isomorphous constituents which mix to form a mineral of complex composition such as tourmaline or epidote; that they are isomorphous mixtures is, of course, firmly held, but the proportionality of atomic volumes is no longer invoked as a criterion, and similarity of composition is now so liberally interpreted that the views of Hermann should no longer be dismissed as wild speculations.

In many of the questions concerning which controversy raged, such as whether only the constituents which enter into the mixtures are to be called mineral species, or whether the intermediate mixtures also deserve that name, Rammelsberg took little or no interest. His business was to supply the solid foundation of fact only to be attained by laborious analyses, upon which alone theory can be based.

In my opinion, the most important contributions which Rammelsberg made to science were those which he made as a mineral chemist. If, as we have seen, he brought to the study of chemistry a much needed knowledge of crystallography, he certainly brought to the study of minerals an even more needed knowledge of chemistry.

He himself deplores the fact that in the early days of the science Haüy was solely a crystallographer and Klaproth a chemist. "What rapid strides would have been made by mineralogy if Haüy's crystallographic knowledge and Klaproth's chemical ability had been united in a single person." It is not often that a science suffers from over specialisation in its early periods, but the study of minerals is not so much a distinct science as a region in which three sciences meet, and few were gifted with the power of mastering all three. No man was better equipped than Rammelsberg to achieve conquests in this unexplored region. His published papers on mineralogical subjects are very numerous (including those on rocks and meteorites, about 300); their results are incorporated in his great treatise, "Handbuch der Mineralchemie," which succeeded the "Handwörterbuch," already mentioned. The first edition of the "Handbuch" was issued in 1860, the second edition in 1875, an "Ergänzungsheft" in 1886, and a second supplement in 1895. Rammelsberg's mineralogical work is so vast that here again in order to form an estimate of its character I propose to select only two or three examples, and to leave his "Handbuch" to describe the remainder.

Augite and Hornblende.—Conspicuous among his early papers are those on the augite and hornblende group of minerals. These two minerals were only distinguished by their cleavage angle and form. Augite was known to be a "bisilicate of lime and magnesia in which part of the bases is replaced by protoxide of iron and part of the silica by alumina"; hornblende was almost the same, "the analyses only

prove that augite usually contains more lime, less alumina, and no hydrofluoric acid, which is peculiar, though in minute proportions, to hornblende" (Allan's "Mineralogy," 1834, p. 149). Augite was made to include the minerals known as augite, diopside, baikalite, fassaite, coccolite, sahlite, and omphacite; hornblende included the species known as hornblende, actinolite, tremolite, asbestos, hedenbergite, and pargasite.

Gustav Rose had proved that augite and hornblende may be referred to the same crystal axes, and urged that they may therefore be regarded as the same mineral; it is true that they have a different cleavage angle, and that the faces that occur upon the one are not found upon the other, so that they present quite a different aspect, but they are sometimes found attached to one another in parallel positions; further, Rose showed that when hornblende is fused, it recrystallises as augite; it was therefore supposed that the temperature at which the mineral was formed may have been sufficient to determine whether it should crystallise with the faces and cleavage of augite, or with the faces and cleavage of hornblende.

Subsequently, Rose himself discovered that a mineral, to which the name uralite was given, possesses the faces of augite and the cleavage of hornblende, and is clearly augite which has been converted into hornblende. The balance of evidence, consequently, inclined again to a separation of these minerals into two distinct species.

The chemical characters were very imperfectly known. Heinrich Rose had found the non-aluminous augites to be simple bisilicates, $RSiO_3$, and therefore analogous in composition to the magnesia silicate hypersthene, whose cleavage is different, and to the lime silicate wollastonite whose angles are not those of augite. The non-aluminous hornblendes seemed from Bonsdorff's analyses to have a different composition, the oxygen ratio of acid to base being more than 2 : 1; they might be regarded as mixtures of the bisilicate $RSiO_3$ with trisilicate $R_2Si_3O_8$, but if so the relative proportions were not constant. Rammelsberg himself was inclined to believe the mineral to be an isomorphous mixture of these two silicates—rather an advanced view of isomorphism for that date. As for the aluminous augites and hornblendes, they were in hopeless confusion.

It was in 1851 that Rammelsberg seriously grappled with this problem of the augite-hornblende group which had confronted him when he drew up his mineral system in 1847. In the first edition of the "Mineralchemie" in 1875, he was able to incorporate no less than 15 analyses of augites and 15 analyses of hornblendes, made by himself. He had already pointed out that some hornblende undoubtedly has the composition of augite, and some augite undoubtedly has the composition of hornblende. He set himself to discover in particular

whether these minerals do not contain alkalis, whether the iron is ferrous or ferric, and to determine the exact proportions of magnesia and alumina which were at that time only separable with considerable difficulty. Not content with isolated analyses, he undertook a complete revision of the whole group. With the help of Gustav Rose and Krantz, the mineral dealer, he provided himself with the very best material of all the available species ; he measured the crystals, revised and recalculated the results of previous observers, and made careful analyses and determinations of the specific gravities, no less than 21 analyses of augites and 24 of hornblendes being recorded.

From the crystallographic point of view, he showed that the lime silicate wollastonite, the soda silicate ægirine, the lime iron silicate babingtonite, and the manganese silicate rhodonite all belong to the same group.

From the chemical point of view, the minerals fall into four groups :

A, containing neither Al nor Fe‴.

B, containing Fe‴, but not Al.

C, containing both Fe‴ and Al.

D, containing Al, but not Fe‴.

Group A contains many augites, and also the light-coloured hornblendes known as tremolite and actinolite.

Pure tremolite is $CaSiO_3 + 3MgSiO_3$.

Pure diopside is $CaSiO_3 + MgSiO_3$.

Group B contains the following :

Augites.	*Hornblendes.*
Acmite.	Arfvedsonite.
Ægirine	
Babingtonite.	

These are mixtures of $R''SiO_3$ with $Fe_2(SiO_3)_3$ in varying proportions. Hence $Fe_2(SiO_3)_3$ is isomorphous with $R''SiO_3$, and therefore also group B is isomorphous with group A. This was a new conception, and, being reluctant at that time to accept Gerhardt's view concerning the two modifications of iron, Rammelsberg was inclined to regard the relation as due to the dimorphism of the oxide, for Fe_2O_3 is found both in a cubic and a hexagonal form among minerals.

Group C.—Here the investigation involved great labour ; special care was required for the separation of aluminium, and the minerals were examined for alkalis and for fluorine. After the analysis of specimens from 15 localities, it was concluded that the aluminiferous augites and hornblendes all contain both FeO and Fe_2O_3, and that all the aluminiferous hornblendes contain K and Na. In previous analyses, the iron had all been reckoned as FeO. It might be

objected that there is no guarantee of the purity of these black, opaque minerals, but Rammelsberg insists that his specimens, although black, are transparent, and are shown by the microscope to be homogeneous. In order to ascertain whether the alumina belongs to the electropositive or the electronegative constituents, he calculated in all the analyses the oxygen ratio for

(1) $RO + R_2O_3 : SiO_2$.
(2) $RO : R_2O_3 + SiO_2$.
(3) $RO + Fe_2O_3 : SiO_2 + Al_2O_3$,

and finding the last alone to be constant and to have the same value for the augites and hornblendes in group C, concluded (1) that augite and hornblende are shown by groups A and B to have the same composition; they must therefore have the same composition in C; and hence (2) Al is an acid and Fe a basic constituent, and the augites and hornblendes are all to be regarded as bisilicates and bialuminates.

Group D contains only spodumene, a lithium sodium aluminium bisilicate in which the aluminium is basic.

In a subsequent paper (1867), Rammelsberg gives up this interpretation and regards the alumina in both the augite and hornblende group as an accessory constituent, Al_2O_3, entering into isomorphous mixture with $RSiO_3$. This idea may be traced to Bonsdorff; it was supposed to be justified by the isomorphism of hæmatite, Fe_2O_3, with ilmenite, $FeTiO_3$.

The subsequent history of these minerals may be added, since it serves to illustrate two features of Rammelsberg's character, his readiness during most of his long career to accept any view which appeared really better than his own, and the conservatism which only overtook him in old age.

In 1871, Tschermak offered an explanation of the aluminiferous augites which was almost universally accepted; their analyses were fully expressed by the formula $mR_2Si_2O_6 + nRAl_2SiO_6$. Subsequently Scharizer offered an explanation of the aluminiferous hornblendes according to which they are mixtures of the mineral actinolite, $CaMg_3(SiO_3)_4$, with a known variety of hornblende having the constitution of a garnet, $R_3Al_2(SiO_4)_3$, to which he gives the name syntagmite. Since the latter can be expressed as $3RSiO_3,Al_2O_3$, it is evident that all such mixtures will agree with Rammelsberg's second hypothesis.

In the second edition of his handbook (1875), Rammelsberg adheres to his old view, but in the Ergänzungsheft (1886) he confesses that Al_2O_3 can hardly be regarded as isomorphous with $RSiO_3$, since Al_2O_3 never has the form of augite, and accepts a more general form of Scharizer's interpretation according to which both augites and hornblendes are isomorphous mixtures of the molecules $RSiO_3$ and

$R_3Al(SiO_4)_3$, and laboriously calculates the various atomic ratios of 56 analyses on this hypothesis.

It is curious that in the second supplement, published in his 83rd year, he should return to his original view and regard Al_2O_3 as isomorphous with $RSiO_3$.

At the present time, Tschermak's explanation is generally made the basis of any speculations upon the constitution of these minerals, but it must never be forgotten that the necessary facts were supplied by Rammelsberg's analyses and by his discovery that they contain both Fe″ and Fe‴.

In any case, whatever explanation be offered, the augite-hornblende group is one of those in which we are driven to accept the intermixture of two molecules having very different constitutions—quite as different as those suggested in other cases by Hermann, whose views are supposed to be long buried and forgotten.

Felspars.—Another example in which such intermixture is perfectly well proved, and even universally accepted, is afforded by the felspar group. The minerals known as albite, oligoclase, labradorite, and anorthite had long been classed together as felspar in spite of differences in composition, but their chemical relations were never understood until Tschermak in 1864 showed that they are not well defined minerals, but pass into each other and that the whole series consists of isomorphous mixtures in varying proportions of the soda-felspar, albite, with the lime-felspar, anorthite. But Rammelsberg had already (in 1850) expressed his conviction that the felspars are an isomorphous group, in spite of the prevalent view that they were distinct minerals. "One and the same type of geometrical form," he says, "scarcely differing more than is usual in isomorphous substances, and a great similarity in all their physical properties unite these minerals which we call in general felspar, and it was only the chemist who found it necessary to separate them because he found that the different members, orthoclase and albite, oligoclase, labradorite and anorthite, cannot be treated as isomorphous by replacement of their individual constituents, but possess compositions which are stochiometrically different, the equivalents of the silica varying in the proportion 12 : 9 : 6 : 4. . . . The observation made upon tourmaline that silicates of different basicity united in different proportions are isomorphous, that is to say, have the same, or nearly the same, form, seems to be repeated in the most important and wide-spread minerals, felspar and mica."

When Tschermak proposed his theory, Rammelsberg, in spite of the opposition of Streng, vom Rath, and others, was the first to give it his warm and undivided support, and here he found a powerful ally in Bunsen. Every subsequent attack upon the theory has only resulted

in its confirmation by renewed analyses, so that at the present time there are no isomorphous mixtures which have been so fully studied, both chemically and physically, and so well established, as those of albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$.

The reason why Rammelsberg was so quick to accept the felspar theory of Tschermak and so reluctant to accept his augite theory is easy to see. In the one case, the two constituents were known to exist, in the other case one of them was hypothetical, and no man was more averse to speculation than Rammelsberg.

In 1872, he published a paper entitled "The Present State of our Knowledge of the Felspars," in which he made an elaborate calculation of all the felspar analyses in order to ascertain how closely they agree with Tschermak's formula. This was followed in 1884 by a paper on "Isomorphous Minerals which are not Chemically Analogous," in which, after mentioning olivine, garnet, tourmaline, epidote, and idocrase as minerals whose constituents are analogous, the author admits that silicon, like molybdenum, tungsten, vanadium, &c., forms acids of different basicity; among these, he prefers to accept only the simpler as independent, and regards the more complex as mixtures of these, for example, $H_6Mo_7O_{24}$ as $2H_2Mo_2O_7 + H_2Mo_3O_{10}$. Thus the only silicic acids of which it is necessary to assume the existence are $H_2Si_2O_5$; H_2SiO_3; H_4SiO_4; H_6SiO_5; and H_8SiO_6.

If a salt contains metals of different valencies, it is to be regarded as a mixture of molecules of the same basicity; thus

$$\text{Anorthite, } CaAl_2Si_2O_8 \text{ is } Ca_2SiO_4 + Al_4(SiO_4)_3.$$
$$\text{Albite } NaAlSi_3O_8 \text{ is } Na_4Si_3O_8 + Al_4(Si_3O_8)_3.$$

But we are driven to regard the salts of H_4SiO_4 as capable of entering into isomorphous mixture with the salts of $H_4Si_3O_8$.

Whatever speculations have subsequently been entertained regarding the felspars and other silicates, I fear we must confess that mineral chemistry has not progressed much beyond this point: it is certain that the anorthic soda-lime-felspars are mixtures of albite and anorthite; it is equally certain that no explanation why they should form isomorphous mixtures is sufficiently complete to supply the clue to all the other complex silicates found in Nature.

Towards the end of his life, Rammelsberg returned to the subject again; one of his last papers, published in 1896, contains a number of fresh calculations made with the object of ascertaining which analyses conform to the theory and which deviate from it.

Other Silicates.—Rammelsberg's memoir of 1884 is really inspired by his work on the minerals known as scapolite, chabazite, and phillipsite, which was published in the same year. Here again he

holds by the principle that we are not justified in assuming a mineral to be a mixture of two or more definite silicates unless we have independent evidence of their existence.

Thus in the scapolite group, according to him, sarcolite is $(R'_4R''_2)_3Al(SiO_4)_3$.

Humboldtilite, Meionite, Wernerite } are $mR'_2SiO_3 + nR'_4SiO_4$.

Marialite is $mR'_2SiO_3 + nR'_2Si_2O_5$.

Tschermak's explanation of these minerals as a mixture of two hypothetical silicates he refuses to accept.

Again, in the chabazite group, after an elaborate criticism of all the analyses which indicates that $R'' : Al_2 = 1 : 1$, he selects the three simplest formulæ :

$$R''Al_2Si_3O_{10} + 5H_2O$$
$$R''Al_2Si_4O_{12} + 6H_2O$$
$$R''Al_2Si_5O_{14} + 7H_2O$$

and shows that all the analyses may be interpreted as mixtures of these three molecules.

Similarly, in the phillipsite group, $R'' : Al_2 = 1 : 1$, and the minerals may be regarded as mixtures of :

$$2R''Al_2Si_3O_{10} + 7H_2O$$
$$2R''Al_2Si_4O_{12} + 9H_2O$$
$$R''Al_2Si_6O_{16} + 6H_2O$$

The theory of Fresenius that the minerals of these two last groups can be represented by $m(R''Al_2Si_2O_8 + 4H_2O) + n(R''Al_2Si_6O_{16} + 6H_2O)$ appears to Rammelsberg a mere speculation, since although one of these silicates has the constitution of desmine the other is hypothetical. His views are best expressed in his own words : "When shall we appreciate the fact that we do not yet know the cause of isomorphism, and that equality of form and analogy of composition do not stand to one another in the relation of cause and effect. Nearly forty years ago, Hermann stated the following law :—in isomorphous compounds which are not analogous in composition, there are always two members at the ends of the series, and from their mixture in varying proportions all the remainder result. This he called Heteromerism and endeavoured to establish his views in numerous papers. By the progress of mineral chemistry, the facts upon which this theory was based have been abundantly discredited, and it has never enjoyed the confidence of chemists because it rests upon hypotheses which cannot be tested by experiment. It was therefore a matter of the greatest scientific importance that Tschermak discovered the law of

mixture in the soda-lime-felspars, and it would be equally important to establish similar laws in other groups in which similarity of form is accompanied by difference in composition. But for this, it is necessary that the terminal members of the series should be really known, and that, as with the felspars, the composition of every mixture should by the atomic ratios of its elements supply a *proof* of the law."

Towards the end of his long life, it was perhaps natural that Rammelsberg should feel himself somewhat out of sympathy with the views of younger chemists. One of the fruitful conceptions in modern mineral chemistry has been that of the mutual replacement of hydroxyl and fluorine which has been brought forward by Penfield and established in the case of several minerals. The first of these was the lithium-aluminium phosphate, amblygonite, in which the proportion of water was found to vary between 1·75 and 6·61, and that of fluorine between 11·26 and 1·75. Penfield showed that in all the analyses $P : Al : R : (F,OH) = 1 : 1 : 1 : 1$, so that if the water be calculated as hydroxyl replaceable by fluorine, the formula becomes quite simple. Wagnerite and triploidite were already recognised as isomorphous.

In 1884, Rammelsberg expressed himself as follows on this view: "The hypothetical atomic group hydroxyl, which plays a great part in modern chemistry, is now beginning to figure in the formulæ of minerals. Penfield having found in some amblygonites less fluorine and more water, regards all these as unaltered compounds in which HO replaces fluorine; according to this, potassium fluoride and potash would be analogous compounds. I have already protested against this highly unchemical view."

Penfield has subsequently confirmed his theory by analyses of herderite, hamlinite, topaz, and other minerals; it enabled him to give to topaz the beautifully simple formula $Al_2(F,OH)_2SiO_4$. But even with these before his eyes, Rammelsberg in the second supplement to his "Mineralchemie" (1895) repeats that the theory is "in hohem Grade unchemisch"; he persisted in regarding the water in topaz as merely due to incipient decomposition.

It must be remarked that a very recent research by Fels, published in the present year, has failed to find any replacement of hydroxyl by halogen elements in the benzene derivatives.

Professor Penfield, in writing to me about Rammelsberg as a mineral chemist, uses the following words:

"He was without question a man of great energy and enthusiasm, and he accomplished an enormous amount of work. When I studied Rammelsberg's early tourmaline papers, I was impressed by the magnitude of the undertaking, and with the excellent character of the work. He made at the outset mistake in deciding that tourmaline had no water, and in assuming that loss

on ignition was SiF_4, and, having once made the mistake, he seemed never to be able to get his analyses into good shape. He revised the analyses from time to time, always changing some of the figures, and no man probably will ever be able to tell just what results Rammelsberg placed most confidence in. He practised a sort of chemical sleight-of-hand work with his results, moulding H_2O and F somewhat to suit his own ideas. I believe that his results, as modified by Foote and me in our paper on tourmaline, and founded on the assumption that the bases were probably determined with a good degree of accuracy, are fairer than any of Rammelsberg's own modifications of his analyses. Although Rammelsberg could be very severe as a critic, he seemed to me to be a man of tender feeling. He took occasion to criticise me at one time, stating that my ideas concerning the composition of amblygonite were *rein unchemisch*. I am willing to admit that following the method adopted by Rammelsberg, and writing the composition of amblygonite $Al_2P_2O_8,2LiF$ with isomorphous $Al_2P_2O_8,2LiOH$ was somewhat *unchemisch*, although I did not intend to convey the idea that amblygonite contained a soluble neutral salt, LiF, and a soluble alkali, LiOH, any more than Rammelsberg intended to convey the idea that apatite contained soluble $CaCl_2$ when he wrote the composition as $3Ca_3P_2O_8,CaCl_2$. It certainly is a decided improvement to write amblygonite $Li(AlF)PO_4$ with isomorphous $Li(Al,OH)PO_4$. On the subject of the isomorphism of fluorine and hydroxyl, he said that he could not bring himself to believe in it. To him, water in topaz, for example, would indicate partial decomposition."

Upon some groups of minerals he held quite peculiar views. The arsenic and antimony compounds of iron, nickel, and cobalt, he regarded as isomorphous mixtures of these elements, in fact as alloys; in one of his last papers (1897), he extends this view to the sulphur which these minerals contain, and explains the whole group either as mixtures R_nA_mS, or as mixtures of this molecule with RS_2. Other instances might be quoted in which his own interpretations of the analyses which he had made have not been generally accepted.

If it was difficult to give a summary of Rammelsberg's work in chemistry on account of the extent of his labours, in mineralogy it is quite impossible; to give a catalogue of the minerals which he analysed would be to mention about two-thirds of the mineral kingdom; they can be extracted from his handbook of mineral chemistry, which contains references to all of them. I have contented myself with mentioning a very few of the more important, and especially such as led to the discussion of general principles. Among those which I have been compelled to pass over are the memoirs on mica, on the borates, the tantalates and niobates, on epidote, idocrase, and a host of other large groups, not to mention tourmaline, which is now the subject of lively discussion between Penfield, Clarke, Tschermak, and others. Rammelsberg published important memoirs on this subject in 1850 and 1870, and returned to it in 1890. I believe that he was engaged upon another memoir on tourmaline at the time of his death.

It is noteworthy that in a science which has suffered terribly from the over-multiplication of names, Rammelsberg was entirely free from this infirmity of intellectual conceit, and probably added fewer mineral names to the literature in proportion to the work which he did than any other mineralogist. In order to emphasise this fact, a list of the new names which he introduced is subjoined :

Antimonial arsenic.	Gotthardite.
Castillite.	Heteromorphite.
Chiviatite.	Hydromagnocalcite.
Chlorapatite.	Magnoferrite.
Crednerite.	Pseudolibethenite.
Cuprodescloizite.	Sigterite.
Epichlorite.	Tachydrite.
Fluorapatite.	Waldheimite.
Ginilsite.	Xonotlite.

Writing to Wolcott Gibbs in 1882, Rammelsberg complains that since the duties of the second professorship at the University had been added to his other occupations he had very little leisure for work ; but his ideas of work and leisure were not those of other men. How, among the numerous investigations to which I have already alluded, he found time for research in other subjects besides mineralogy, is hard to understand. There are yet two other important branches of his work which must not be overlooked. In Humboldt's "Cosmos," he is alluded to as "a sagacious chemist who has recently devoted himself uninterruptedly, and with equal activity and success, to the analysis of aerolites," and numbers of his memoirs relate to the analysis of meteorites. Another considerable group of his published papers contain laborious rock analyses ; and in 1854 he had made for Humboldt an analysis of the trachyte of Chimborazo. A paper published in 1847 dealt with the inorganic materials contained in plants. Before middle life, he had attained the reputation of being the most experienced inorganic chemist in Europe. Among the letters which he received are to be found requests from Brooke, Miller, and Lettsom, in England, that he should analyse minerals which they had discovered ; from Schliemann, in Germany, that he should determine the composition of metals from Ilios ; from Lawrence Smith, in America, that he should introduce certain methods of silicate analysis into Germany ; from Grailich, in Vienna, that he should supply him with crystals of the substances which he had analysed. Many of his papers were translated into other languages as soon as they appeared.

Writing in 1852, James Dana says, "Your researches are to me always the highest authority." And again, in 1876, "Your 'Handbuch' gives me anew an exalted idea of the value of your labours for the

progress of mineralogical science. I have carried forward my studies so much of the time with your book in hand that I feel as if I had always enjoyed your companionship and your personal aid, and I may add that it was this aid which made my work possible."

Senarmont, in 1855, cannot refrain from writing to the author of the "Handbook of Crystallographic Chemistry," although he does not know him personally, to express his appreciation of its great value, and his desire to assist Rammelsberg in these labours, in which, he is sure, Marignac joins him.

Marignac himself, in 1881, referring to the second edition, writes, "You have already rendered chemists a great service in your preceding work by giving them everything relating to the crystalline form of chemical compounds, but the service is still greater now that you have added a description of all the physical properties. This must have involved immense labour, and science will always owe you a debt of thanks."

In addition to his own treatises and memoirs, Rammelsberg published translations of Dumas' "Philosophie der Chimie," of Percy's "Metallurgy," and of several papers, such as that of Berzelius on mineral classification, and of Scacchi on polysymmetry.

It would be inconceivable that one man could accomplish all the work which I have now surveyed without assistance, even in a long lifetime, and many of the mineral analyses which issued from Rammelsberg's laboratory were made wholly or in part by his assistants. I find in his treatise on mineral chemistry the names of more than 60 assistants or pupils mentioned as responsible for the analysis of as many minerals; his own analyses are, of course, far more numerous. This will serve to indicate the activity of his laboratory and at the same time, perhaps, the fact that his heart was always really more in the development of research than in the routine work of education; in fact, I do not think that he ever undertook much of the personal supervision of the laboratory during the later part of his career.

I have quoted Professor Liveing's recollection of Rammelsberg as he was in the early prime of life. Dr. Liebert, who worked with him towards the end of his career as a teacher, tells me that the name of Rammelsberg always recalls to his mind the vision of a little man, with his head thrust half into the balance case, rapidly changing the weights with a quick, nervous action. All such operations he conducted with extraordinary rapidity. He was never without a cigar held in the corner of his mouth, and always encouraged his students to smoke in the laboratory. At that time he was still engaged in analytical work, although his hand shook so much that he used a silver wash-bottle for fear of breakage. Dr. Liebert says that he was

extraordinarily accurate in his lectures, and very rarely showed that absent-mindedness (Zerstreutheit) which is a proverbial failing of German professors; he recalls only one occasion on which Rammelsberg lost his equilibrium. "He was lecturing on the oxygen compounds of nitrogen. As usual, the demonstrator had prepared the different experiments beforehand. All went well until nitric oxide was reached; the Professor had stated that vividly burning bodies undergo further combustion when brought into contact with this gas, and proceeded to illustrate this by experiment. Having first introduced several heated metal wires which burnt with a vivid light, and having repeated the experiment with potassium and burning phosphorus, he finally asked for sulphur, which he ignited and introduced into the gas. The flame was quickly extinguished. Rather irritated, he repeated the experiment—with the same result! Rammelsberg prided himself on his accuracy, and began to grow vexed at the repeated failure. With an angry glance at the demonstrator he demanded flowers of sulphur. The result was the same. This was too much for Rammelsberg's patience; turning abruptly to the demonstrator, he said in an 'undertone' distinctly audible to all, 'You have made a mistake; this carelessness will not do,' and turning to his audience, apologised for the mistake which his demonstrator had made in preparing the wrong gas.

"When the demonstrator repeated the process after the lecture, and compared what he had done with the notes of Rammelsberg's handbook, he found the explanation of 'his' mistake. The statement in the notes was:—vividly burning bodies undergo further combustion in NO (examples enumerated); burning sulphur is extinguished."

Among the many chemists or mineralogists who at different times worked with him are to be mentioned Liveing, Wolcott Gibbs, Groth, Max Bauer, Rüdorff, Friedheim, Stahlschmidt, Philipp, and Schöne.

As a lecturer and teacher he was, according to the testimony of all his pupils, admirably lucid and thorough; but what seems to have impressed them most was his indomitable energy in research; he would spare no trouble in repeating the experiments of others; he would spend weeks, or even months, in ascertaining by practical experience the best methods before entering on a difficult analysis; he was supremely careful in obtaining the best possible mineral specimens for analysis; many of them he must have been obliged to purchase for himself at a considerable cost. Mineral chemistry has suffered much in the past from the fact that early analyses were made upon indifferent material, and that there is usually no evidence to show exactly what was used for analysis. Rammelsberg's analyses have never been doubted, his material was beyond reproach, and it is

satisfactory to know that the original specimens which he employed are now in the Berlin Museum fur Naturkunde; I have little doubt that any further research which may ever be done upon these specimens will only tend to confirm the accuracy of his work, which was maintained until he became too old to carry out analysis at all. Even the very last of his published analyses, those of tourmaline, are quoted with high approval by Penfield, and were regarded by Rammelsberg himself as among his very best.

His labours met with full recognition abroad, and he was an honorary member of more than thirty scientific societies.

It only remains to mention the simple events of his life subsequent to the point at which it was left above, namely, the year 1874, when he was made ordinary Professor of inorganic chemistry in the University of Berlin. In 1859, he had married his second wife, the daughter of the well-known naturalist, Chr. G. Ehrenberg; by her he had two sons and one daughter, all of whom survive him. In 1883, he ceased to be Professor at the Gewerbe-akademie (which was transferred as the Technische Hochschule to Charlottenburg), and was made Director of the newly-founded second chemical institute of the University. There was much discussion concerning this appointment, to which Kopp might possibly have been elected, but it was felt that the director of a teaching laboratory ought to be pre-eminently a practical analyst, and no one had higher qualifications in this respect than Rammelsberg.

All his subsequent work was carried on in this laboratory, where his mineral analyses were continued uninterruptedly for nine years.

In 1891, owing to failing eyesight, he retired from all the appointments which he held, and resided quietly for the remainder of his life at Gross Lichterfelde, in the neighbourhood of Berlin, in a house which he had built adjoining that of his married daughter.

In 1892, he underwent an operation which restored his vision, and he was able to devote himself for the next seven years to the recalculation of mineral formulæ and the writing of the second supplement to his "Mineralchemie;" in this he was aided by the care of his loving wife, to whom he dictated much of his latest work. The evening of the old man's life was a happy and peaceful close to an honourable and active career; his ambitions were realised; his family was settled in life; his faculties were unimpaired. Even now, although he was troubled by frequent headache, the veteran chemist was never idle, but when lying on the couch in his library would call his wife from the next room and dictate to her the thoughts which entered his mind.

Professor Penfield, one of the leading representatives of the modern school, has told me of a visit which he paid to Rammelsberg in his

old age, when he had begun to feel himself out of touch with the younger school of mineral chemists. It was an interesting occasion for both, and to my mind it marks a chapter in the history of mineralogy: the termination of the old rigid reading of isomorphism and the introduction of wider views concerning replacement which are destined to simplify the interpretation of mineral analyses. Professor Penfield writes: "It was in the summer of 1894 that I saw him, when he was 81 years old. He was living a very quiet life at Gross Lichterfelde, near Berlin, and his home seemed to be an ideal one for an elderly man. He was at that time still engaged in scientific work, although he was not strong enough to do very much. He presented me, for example, with a copy of one of his recent articles, in which he criticised my views concerning the chemical composition of staurolite, and he showed me the manuscript for the completion of his "Mineralchemie," which was printed one or two years later. I especially enjoyed hearing him tell of Berzelius, the Roses, and men of that generation, for he knew them well and appreciated their qualities. . . . He said that it was a keen pleasure for him to differ from others; it added a certain spice and zest to life to have and hold scientific opinions at variance to those of others. He certainly was a most friendly and genial old gentleman."

It is pleasant to think of the old man softened in character but still retaining the fierce love of battle and adhering doggedly to his views.

Those who knew him towards the close of his life were most impressed by his extraordinary juvenility; he possessed a power of work, a keenness of debate, and a freshness of memory which few retain at such advanced years. His power of concentration enabled him to work undisturbed and rapidly among any distractions. Even when he was an old man, the presence of his little grandchildren was no hindrance to him while writing.

His interest was throughout his life so centred in his scientific work that he had few relaxations, and did not take much interest in general literature; books of travel were his chief delight. He possessed an extraordinarily retentive memory, and astonished his friends by his knowledge of the facts of history and geography; his acquaintance with modern languages was extensive.

In early life he travelled a good deal during his vacations, but always made the best use of his time for scientific purposes, studying the geology of the countries in which he stayed, and collecting minerals for analysis. One of his early journeys was to Sweden (1844), and for the purpose of visiting Berzelius; another (1867) was a geological tour in Auvergne, in company with the well-known mineralogist,

Professor Sadebeck; he was twice sent to Paris (1855 and 1867) by the Government to act as a representative at international exhibitions. Only in later life were his journeys made as pleasure trips.

His keenness of memory and juvenility of mind remained to the end of his life, and he found great pleasure in recounting reminiscences of his travels and of the men whom he had known. Writing to Wolcott Gibbs in 1893, he says, "I have left my 80th year behind, and have for the last two years given up all educational work. Except, however, for the weakness of old age, I feel myself to be active both in mind and body."

It was not till he had attained the age of 86 that the peaceful and industrious evening of his life was brought to a close. He had never completely recovered from an attack of influenza which had prostrated him a few years previously; in the winter of 1899 he was thrown back by an attack of bronchial catarrh, and on the 28th of December sank to final rest from his labours after a life of unexampled industry.

His character recalls irresistibly the spirit of Browning's grammarian:

> "He knew the signal and stepped on with pride
> Over men's pity,
> Left play for work and grappled with the world
> Bent on escaping.
> 'What's in the scroll,' quoth he, 'thou keepest furled?'"

The great men of genius when they die leave the example of a life which all can admire but to which few can attain; the men of great talent, like Rammelsberg, who make unceasing use of their powers, and by a life of industry contribute, perhaps, equally to the increase of knowledge, leave an equally valuable legacy, an example that all can emulate.

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RAOULT MEMORIAL LECTURE.

(Delivered on March 26th, 1902.)

By J. H. van't Hoff, Member of the Prussian Academy of Science, and Professor in the University of Berlin.

The foreign honorary member whom the Chemical Society lost a year ago, although of an amiable, social character, seems to have been a man of retiring disposition. He rarely left France, and for the larger part of his life lived in that somewhat out of the way town, Grenoble.

Raoult's life thus offers little of attractiveness; it is not romantic; yet, after many years of work, the romance of his life was that almost sudden rise to fame, spreading from this nearly unknown corner, first over the frontier of his country, and then back to France, which made him one of the most prominent men of science of his age.

François-Marie Raoult, born on the 10th of May, 1830, in Fournes, in the département du Nord, in France, was of modest origin, his father having been an employé des Contributions. It was intended that he should enter the Bureaux de l'Enrégistrement, but this career did not satisfy his aspirations, so he left the Enrégistrement and obtained permission to go to Paris, there to pursue his studies. Without fortune or patronage, young Raoult was a student struggling for a livelihood, unable to finish his studies without himself providing the means.

So he gave up studying at Paris, some years later, in 1853, after presenting to the *Académie des Sciences* a short communication, probably his first, containing observations on the transport of electrolytes by the action of the galvanic current as well as on electrical endosmosis (*Compt. rend.*, 1853, **36**, 826). Characteristic of the circumstances in which he pursued these investigations are his concluding words: "Je laisse à d'autres plus fortunés que moi le soin de mener la science plus avant dans la voie nouvelle que je viens de lui ouvrir."

It was in the same year, 1853, that Raoult accepted the appointment of *Aspirant répétiteur* in the Rheims Lycée, becoming in 1855 *Régent de physique* in the College of St. Dié; in 1856, *Professeur adjoint*, and subsequently *Chargé de cours de physique* in Rheims again; in 1860 in Bar-le-Duc; his leisure having been employed in obtaining his degree as *Licencié ès-sciences physiques* and *Agrégé de l'Enseignement secondaire spécial*. In 1862, he left Bar-le-Duc for a corresponding position in Sens, and in this small country town, with no intellectual resources, left to his own initiative amid adverse material surroundings, forced

by want of means to construct his own apparatus, he prepared the *Thèse* on electromotive force for which, in 1863, he obtained his degree in Paris of *Docteur ès-sciences physiques.*

With this publication, Raoult began his scientific career, which may be divided into three distinct periods, physical, chemical, and physico-chemical.

Raoult as a Physicist.

The above-mentioned thesis at once characterises Raoult as an accurate and independent investigator, already in advance of his age in conclusions founded on careful examination of fact.

Firstly, employing different galvanic cells of the Daniell type, Raoult measured the heat due to the chemical action (*chaleur chimique*) and that due to the electric work produced (*chaleur voltaïque*). Contrary to the opinion then adopted, he found that these two values were by no means identical; in some cases, as in the ordinary Daniell cell, Cu | $CuSO_4$, $ZnSO_4$ | Zn, both practically correspond, for each is about 23·6 cal. for a gram-equivalent (the most exact recent measurement gave 24·8); in an analogous cell, Cu | $Cu(NO_3)_2$, $AgNO_3$ | Ag, however, the "chaleur chimique" amounted to 16·4, whereas the "chaleur voltaïque" was only 7·8. Keeping as closely as possible to the direct results of experiment—a characteristic of Raoult's way of working—he closes this communication with a mere question: "Pourquoi cette différence? Voilà une difficulté sérieuse digne de l'attention des physiciens."

A second part of this research was devoted to decompositions produced by a galvanic current in the so-called voltameter. Raoult studied especially the heat development accompanying decompositions, explaining it by the excess of heat corresponding to the electric work done in the voltameter over the heat absorbed by the chemical change produced, in this way applying to the voltameter the principle underlying his discovery of the difference between the two values found for the cell. Thirdly, this conception enabled him to determine indirectly the heat absorbed by the chemical change which occurs in the voltameter. It was thus, for example, that he found the heat absorbed in decomposing 9 grams of water to be 33·8 cal., whereas Favre and Silbermann found the heat developed in the formation of the same amount of water to be 34·5 cal.

The conclusion to his two papers on this subject (*Ann. Chim. Phys.*, 1864, [iv], 2, 317; 1865, [iv], 4, 392) may be given in his own words:

"J'ai, le premier, mesuré et comparé la chaleur chimique et la chaleur voltaïque des piles."

"J'ai découvert les véritables lois qui président au dégagement de la chaleur dans les voltamètres."

"J'ai donné le premier moyen de mesurer la chaleur dégagée ou absorbée dans les actions chimiques accomplies sous l'influence des courants électriques."

In his further investigations on electro- and thermo-chemistry, Raoult liked to come back to that same question of difference between voltaic and chemical heat which he considered to be fundamental. A very striking proof of the non-identity of the two was given in the fact established by him (*Compt. rend.*, 1869, **68**, 643) that solid and liquid metals, at the temperature of fusion, produce in the cell the same electromotive force; he insisted on this especially in the case of bismuth, which metal, having a latent heat of fusion corresponding to 1·327 cal. for an equivalent of 105 grams, ought to produce in melting a difference in electromotive force of 0·055 Daniell.

A second indication in the same direction is not less valuable. Finding that the electromotive force in a Daniell cell increases on diluting the solution of zinc sulphate surrounding the zinc, but decreases on diluting that of the copper sulphate (*ibid.*, 1869, **69**, 823, 826), he insisted on the conclusion that in taking a saturated solution of zinc sulphate and so increasing the heat development of the reaction by that arising from the crystallising out of the solid sulphate, the electromotive force changes in the opposite sense and becomes smaller.

Raoult's attention being claimed by other pursuits, it was in 1870 that he summed up his views in a very interesting paper on the difference between voltaic and chemical heat (*Bulletin de la Société de Statistique de l'Isère*). He concluded that in the galvanic cell two different kinds of change take place, the one incapable, the other capable, of producing electromotive force. Those incapable are changes of state of aggregation, such as melting and dissolving; those capable are chiefly chemical change and change in concentration.* We now see how far Raoult had already gone in the right direction and how some further experiments on this influence of concentration, and especially how an application of theoretical considerations, might have led him to a definite solution of the problem.

* Dans les éléments voltaiques analogues à celui de Daniell, la désagrégation chimique des corps et leur diffusion dans l'eau, de même que les actions inverses ne participent en rien à la production du courant électrique, et ce sont les seules actions qui sont dans ce cas.

Raoult as a Chemist.

It was while he was carrying out this electro- and thermo-chemical research, in which many new facts and relations came to light, and on which, perhaps, it is not necessary to dwell on this occasion, that Raoult entered the *Faculté des Sciences de Grenoble*, in 1867, as *Chargé du cours de chimie*, being promoted, in 1870, to the Chair of Chemistry as successor to Leroy. This chair he occupied until his death on April 1st, 1901. From this time, a change is visible in the direction of Raoult's work, as he devoted himself more to purely chemical investigation, although he always had a tendency to look at the physical side of every problem.

This change in the field of Raoult's investigations explains how the hitherto continuous character of his work gave place to one of greater variety.

We now find Raoult occupied in examining the gas evolved by a "Fontaine ardente," at St. Barthélemy, near Grenoble, and proving it to be merely methane; next as a judicial expert we see him prove the presence of zinc and copper as normal constituents of the human liver, especially in advanced age (*Compt. rend.*, 1877, **85**, 40). The absorption of ammonia by ammonium nitrate he studied simultaneously with, but independently of, Divers (*ibid.*, 1873, **76**, 1261), and further, he recommended the use of retort-carbon as a means of preventing irregular boiling in the distillation of sulphuric acid. He also demonstrated the inverting action of light on sugar (*ibid.*, 1871, **73**, 1049). Then we find him studying the influence of carbon dioxide in air on respiration with the interesting result that it diminishes the production of the gas, this effect, however, being counteracted by the increased pulmonary action (*ibid.*, 1876, **82**, 1101). Lastly, aiming probably at a lecture experiment, Raoult investigated the formation of a basic carbonate of lime, $CaO,CaCO_3$, produced by heating calcium oxide in carbon dioxide (*ibid.*, 1881, **92**, 189, 1110, 1457) which compound has probably played a part in Debray's work on dissociation and has the property of setting like gypsum after addition of water. Medals made with this material, which has the properties of gypsum but is somewhat harder, were presented by Raoult to the French Academy.

This was Raoult's last purely chemical publication, for he had now found the right direction in which he was to go until death put an end to his labours.

Raoult as a Physico-chemist.

It was in 1878 that Raoult's first publication on freezing points appeared (*Compt. rend.*, 87, 167). This was merely of an empirical character, and pointed to the proportionality (already indicated by Guldberg) between lowering of freezing point, lowering of vapour pressure, and rise of boiling point. Raoult thus entered at once into an investigation of the two subjects which were to form the corner-stones of his fame. As he himself afterwards relates, the lowering of vapour-pressure formed the primary subject of study, and I suppose that, finding the difficulty of determining the strength of alcoholic solutions by measuring their boiling points or vapour-pressures because of the volatility of alcohol, he applied himself to the indirect method of determining the freezing points. At all events, his next paper (*ibid.*, 1880, 90, 865) is devoted to the freezing points of mixtures of alcohol with water. He determines the proportionality between the lowering of the freezing point and the percentage of alcohol present in the solvent, thus stating for this mixture the law which Blagden had found for solutions of inorganic substances. That this stood in close connection with practical application is obvious from the list of alcoholic liquids added to the paper, beginning with cider and ending with Marsala, indicating that their freezing points ($-2°$ and $-10{\cdot}1°$) were fairly proportional to their alcoholic strength. Moreover, he pointed out that a wine may be strengthened by freezing out part of the water.

Having by a happy stroke of luck passed from the investigation of ethyl alcohol to other alcohols and from these to other organic substances, which had not been examined by Blagden, by Rüdorff, or by de Coppet, and having introduced de Coppet's conception of molecular depression, Raoult as early as 1882 attained a wider view of the subject, and published his now historical table of 29 organic compounds (*Compt. rend.*, 1882, 94, 1517) (see next page).

Following Raoult's conclusion, it is obvious from this table that the product obtained by multiplying the depression for a solution containing 1 gram of substance in 100 grams of water by the molecular weight of the dissolved substance, is a constant:

$$\frac{C}{P}M = K,$$

where C stands for the depression caused by P grams in 100 grams of water, and K the molecular constant.

It is astonishing how easily Raoult abandons the narrower view of

Substance.	Formule.	Poids moléculaire.	Abaissement du point de congélation par gramme de substance dans 100 gr. d'eau.	Produit du poids moléc. par l'abaissement dû à un gramme de substance.
Alcool méthylique	$C_2H_4O_2$	32	- 0·541°	17·3
,, éthylique	$C_4H_6O_2$	46	0·376	17·3
,, butylique	$C_8H_{10}O_2$	74	0·232	17·2
Glycérine	$C_6H_8O_6$	92	0·186	17·1
Mannite	$C_{12}H_{14}O_{12}$	182	0·099	18·0
Sucre interverti	$C_{12}H_{12}O_{12}$	180	0·107	19·3
,, de lait	$C_{24}H_{24}O_{24}$	360	0·050	18·1
,, de canne	$C_{24}H_{22}O_{22}$	342	0·054	18·5
Salicine	$C_{26}H_{28}O_{14}$	286	0·060	17·2
Phénol	$C_{12}H_6O_2$	94	0·165	15·5
Pyrogallol	$C_{12}H_6O_6$	126	0·129	16·3
Chloral (hydraté)	$C_4HCl_3O_2+H_2O_2$	165·5	0·114	18·9
Acétone	$C_6H_6O_2$	58	0·294	17·1
Acide formique	$C_2H_2O_4$	46	0·419	19·3
,, acétique	$C_4H_4O_4$	60	0·317	19·0
,, butyrique	$C_8H_8O_4$	88	0·212	18·7
,, oxalique	$C_4H_2O_8+2H_2O_2$	126	0·182	22·9
,, lactique	$C_6H_6O_6$	90	0·213	19·2
,, malique	$C_8H_6O_{10}$	134	0·139	18·7
,, tartrique	$C_8H_6O_{12}$	150	0·130	19·5
,, citrique	$C_{12}H_8O_{14}+H_2O_2$	210	0·092	19·3
Éther	$C_8H_{10}O_2$	74	0·224	16·6
,, acétique	$C_8H_8O_4$	88	0·202	17·8
Acide cyanhydrique	$HAzC_2$	27	0·718	19·4
Acétamide	$C_4H_7AzO_2$	59	0·301	17·8
Urée	$C_4H_4Az_2O_4$	60	0·286	17·2
Ammoniaque	AzH_3	17	1·117	19·9
Éthylamine	C_4H_7Az	45	0·411	18·5
Propylamine	C_6H_9Az	59	0·312	18·4

practical application for the wider scientific horizon, and instead of a list of ciders and Marsalas, an expression like this occurs:

"Cela tend à montrer que, dans la plupart des cas, les molécules des composés organiques sont simplement séparées par l'acte de la dissolution et amenées à un même état, sous lequel elles exercent la même influence sur les propriétés physiques de l'eau."

Of course Raoult does not omit to indicate that a new mode of determining molecular weights may be founded on freezing point experiments.

Two more papers appearing in the same year (*Compt. rend.*, **95**, 187, 1030) show that Raoult's general formulation of the freezing point law for solutions holds not only for water but also for other solvents.

Each solvent has its molecular constant which, in some cases, prob-

ably owing to the formation of double molecules by the dissolved substance, may be reduced to half the normal value. These constants are proportional to the molecular weight of the solvent (M_1), being on an average:

$$\frac{K}{M_1} = 0{\cdot}62.$$

Raoult's data are as follows:

Substance.	K.	M_1.	K/M_1.
Acetic acid	39	60	0·65
Formic acid.....	28	46	0·61
Benzene	49	78	0·63
Nitrobenzene	68	123	0·55
Ethylene dibromide	117	188	0·62
Water	37	3 × 18	0·69

We observe the assertion by Raoult that the constant 18·5 for organic compounds in water is abnormal and is due to the formation of double molecules, whereas the molecular weight of water as a solvent is taken as 54, and is due to a polymerisation in the liquid state corresponding to $(H_2O)_3$.

Cryoscopy. Inorganic Compounds.

Having thus obtained an insight into the laws governing organic compounds, Raoult enters the more difficult field of salt solutions, in which a good deal had already been done by Rüdorff and de Coppet, who nevertheless had not reached any general conclusions.

Raoult took acids and bases as intermediate links and found that strong monobasic acids, like hydrochloric acid, and strong mono-acid bases, like potassium hydroxide, have a molecular depression (37) double that of the weaker ones and of organic compounds (18·5). On this observation he founded a neat method of determining the amount of substitution which takes place when a strong acid or base acts on the solution of the salt of a weak one (*Compt. rend.*, 1883, **96**, 560, 1650; **97**, 941).

The next year (1884) witnessed the publication of his systematic researches on the behaviour of salts, and it is curious to observe, by the way, that at this stage of his inquiry Raoult first adopted the new atomic weights and thereby the system of Avogadro, which, it might almost be said, he had unconsciously adhered to for more than two years. His first paper on salts (*Compt. rend.*, 1884, **98**, 509) still contains the formula KNO_6 for saltpetre, but in the next (*ibid.*, 1047; **99**, 324), he adopts the values H = 1, O = 16. The amount of systematic work done in this short space of time is astonishing, the different groups of salts being taken one by one in the order of the valency of

their metals and the basicity of their acids, and, grouping them in this happy way, Raoult reaches at once the general and unexpected result that the molecular depression of salts, strong acids, and bases can be calculated by a summation of numbers, relating to their radicles:

Univalent negative radicles.....	(Cl,Br,OH,NO_3)...	20
Bivalent „ „	(SO_4,CrO_4,CO_3) ...	11
Univalent positive „	(H,K,Na,NH_4) ...	15
Bi- and poly-valent positive radicles	(Ba,Mg,Al_2)	8 *

Applying the method of calculation, for example:

for KOH we get $15 + 20 = 35$, instead of 35·3 found.
for Al_2Cl_6 „ $8 + 6 \times 20 = 128$, „ 129 „

Let me state this in Raoult's own words in order to show in what an impartial and objective way his own conviction is subordinated to fact:

"Ces faits prouvent que, contrairement à ce que j'avais cru jusqu'ici, la *loi générale de congélation* ne s'applique pas aux sels dissous dans l'eau . . .; par contre, ils tendent à montrer qu'elle s'applique aux radicaux constitutifs des sels, à peu près comme si ces radicaux étaient simplement mélangés dans les dissolutions."

As mentioned by Raoult, this additive character had been found by Favre and Valson to apply to the density, and by Hugo de Vries to the osmotic pressure of salt solutions.

An application of these results is made in deciding whether a double salt exists in solution as such, or is split up into its components, the former being the case, for example, in such a compound as sodium platinichloride, and the latter for the alums (*Compt. rend.*, 1884, 99, 914). Most important, however, is the fact that from this time dates the great international co-operation in the field which Raoult had opened.

Whereas Raoult's early work on electromotive force and heat-development lay fallow, because the theoretical conceptions to which they could be attached were only developed about fifteen years later, it was an extraordinarily happy coincidence that his freezing point investigations met with corroborative theoretical views, which could only enhance the high value already attached to Raoult's achievements.

His first work on electromotive force, although important in character, left Raoult's name almost unknown, because it appeared at least ten years too soon, and was therefore overlooked when the stream of general development reached that field. Raoult at this period was

* In Raoult's *Cryoscopie* (1901), these numbers are 19, 9, 16, 8, respectively, the last number for bivalent radicles only.

Officier d'académie (1865), and *Officier de l'Instruction publique* (1872), and had received the *Médaille des sociétés savantes* in 1872.

The work on cryoscopy came just at a time when an ardent activity was developing in different countries and from different points of view. Victor Meyer in Germany and Paternò in Italy applied Raoult's method of determining molecular weights as early as 1886; de Vries has already been quoted; then came the theory of solutions, developed by Arrhenius in Sweden and by myself in Holland, and then the great support lent by Ostwald in his *Zeitschrift für physikalische Chemie*, in which Raoult at once took part with enthusiasm, as the facsimile of his letter published with this lecture proves. Rarely has science seen such international interest centred on one problem, and Raoult stood at once foremost, in the position of great advantage belonging to the man who relies on fact in the first instance, and is eager for generalisation, absolutely independent in his opinions, and open to every achievement on his way.

An unbroken series of distinctions now showered down on Raoult, beginning in 1888 with the *Prix international de chimie La Caze*, followed by the Davy Medal in 1892, *Correspondent de l'Institut* in 1890, and honorary or foreign Fellow of the Society of Rotterdam in the same year, of the Literary and Philosophical Society of Manchester in 1892, of the Chemical Society of London in 1898, and of the Academy of St. Petersburg in 1899. In 1900, he was crowned with the Commandership of the Légion d'honneur, a distinction which gave him the highest gratification.

Cryoscopy. Theory of Solutions.

In the meantime, in 1892, Raoult recommenced his freezing point investigations, which had been interrupted in 1884, but now received a new direction with special relation to the theory of solutions. As is well known, this theory treats of the laws governing extreme dilution, and assumes that it is possible to calculate Raoult's freezing point constants under these conditions. We therefore see him occupied in accumulating experimental data for these conditions with the accuracy and impartiality so characteristic of his work.

Let us notice that at first Raoult deemed the molecular constant 18·5 found for organic compounds in aqueous solution to be abnormal, and assumed 37 as the normal value, thus considering organic compounds to be present in the form of double molecules (*ibid.*, 1882, **95**, 1030). It was natural to try, from this point of view, whether extreme dilution would not break down those double molecules and consequently double the molecular constant. A first series of experiments made with cane sugar (*Compt. rend.*, 1892, **114**, 268,

440) seemed favourable to this view, and extreme dilution appeared to show an increase in the molecular constant up to 20·9. As, however, ethyl alcohol did not show an analogous increase (*ibid.*, 1897, **124**, 851, 885), the experiments with cane sugar were again taken up with increased precautions (*ibid.*, 1897, **125**, 751) and, by a small extrapolation, gave 18·7 as the limit for extreme dilution, alcohol giving 18·3. At the same time, Raoult examined sodium and potassium chlorides with the utmost care, and finding, as the limiting values, 37·4 and 36·4 respectively, he openly declared himself in favour of the new theory of solutions:

"En définitive, il est maintenant démontré, pour moi, que les abaissements moléculaires du chlorure de potassium et du sucre, comme ceux du chlorure de sodium et de l'alcool, ont des valeurs limites conformes aux prévisions de M. Arrhénius."

In the summary of his work in this direction (*Cryoscopie, Scientia*, No. 13, 1901), written in the last year of his life, Raoult grants all the conclusions of the theory of solutions, but as a thoroughly experimental investigator he objects to build it up on that large but hypothetical principle called the extended law of Avogadro. He consequently prefers generalisation, and in such a sense expresses his views on solutions as follows in concluding a lecture at the Paris International Congress of Chemistry in 1900. "À une même température l'acte de la dissolution et celui de la vaporisation réduisent chaque corps en particules, qui ont la même masse et la même force vive de translation à l'état dissous et à l'état gazeux."

Vapour-pressure.

We now come to the parallel series of experiments on vapour-pressure which Raoult executed. As has been observed, it was the proportionality between the rise of boiling point, the lowering of vapour-pressure, and the depression of freezing point, which first led Raoult to his freezing point investigations. It was the fertility of this field which brought him back to a study of vapour-pressure once more.

As had already been proved in some cases by Wüllner, Raoult found proportionality to exist between the lowering of the vapour-pressure $(f-f')$ and the pressure (f), at least for dilute solutions, and hence the relative lowering of pressure

$$\frac{f-f'}{f}$$

is independent of temperature.

The second step was to prove the consequence of proportionality between the lowering of vapour-pressure and of freezing point and to

test the constancy of the so-called molecular lowering which was found (*Compt. rend.*, 1886, 103, 1127; 1887, 104, 967) and could be expressed by

$$\frac{f-f'}{fP}M = K,$$

where, as before, P is the number of grams of substance dissolved in 100 grams of the solvent, and M its molecular weight.

The third step was fundamental and may be considered as the happiest generalisation which Raoult reached (*Compt. rend.*, 1887, 104, 1430). It was indicated by the results of freezing point determinations in which Raoult had hoped to detect proportionality between molecular lowering and the molecular weight of the solvent (a relation, however, which did not prove to be general). The molecular lowering of vapour-pressure was therefore compared with the molecular weight of the solvent, with results which are shown in the following table:

Dissolvant.	Poids moléculaire du dissolvant M'.	Diminution moléculaire normale de tension K.	Diminution de tension produite par 1 mol. dans 100 mols. $\frac{K}{M'}$.
Eau	18	0·185	0·0102
Chlorure phosphoreux	137·5	1·49	0·0108
Sulfure de carbone	76	0·80	0·0105
Bichlorure ,, (CCl_4).	154	1·62	0·0105
Chloroforme	119·5	1·30	0·0109
Amylène	70	0·74	0·0106
Benzine	78	0·83	0·0106
Iodure de méthyle	142	1·49	0·0105
Bromure d'éthyle	109	1·18	0·0109
Éther	74	0·71	0·0096
Acétone	58	0·59	0·0101
Alcool méthylique	32	0·33	0·0103

Raoult formulates the relation thus found as follows: "1 Mol. de substance fixe, non saline, en se dissolvant dans 100 mol. d'un liquide volatil quelconque, diminue la tension de vapeur de ce liquide d'une fraction à peu près constante de sa valeur et voisine de 0·0105," that is,

$$\frac{K}{M_1} = 0{\cdot}0105.$$

It was this conclusion that at once brought Raoult into relation with my theory of solutions (*Bihang K. Svenska Vet.-Akad. Handl.*, 1886, 21, No. 17), with which it is in agreement, as Raoult himself states (*Compt. rend.*, 1887, 105, 859):

"L'accord entre l'expérience et la théorie est donc, sur tous les points, aussi complet qu'on peut le désirer en pareille matière."

It was the investigation of this law which Raoult pursued in detail in the latter part of his life; he found it to apply also to salts such as sodium chlorate, potassium acetate, sodium acetate, lithium chloride, lithium bromide, potassium thiocyanate, calcium nitrate, calcium chloride, and mercuric chloride, at least in alcoholic solution, in which they behave as non-electrolytes (*Compt. rend.*, 1888, **107**, 442), whereas in aqueous solution they behave, to use his own words, "comme s'ils étaient décomposés en leurs *ions*."

But the best part of his work was still to be done, in cooperation with Recoura (*Compt. rend.*, 1890, **110**, 402; 1896, **122**, 1175). In using acetic acid, and afterwards formic acid, as a solvent, Raoult found that K/M_1 had a value of about 0·0161, instead of 0·0105, and at once attributed the discrepancy to the abnormal vapour density of acetic acid (which again is involved in the theory of solutions, as M_1 means, on this basis, the molecular weight of the solvent as derived from the density of its saturated vapour), a number which also exceeds the normal value by about 60 per cent. It was on this account that, in a later publication (*ibid.*, 1893, **117**, 833), he gave this most general and exact expression for his vapour-pressure observations:

$$\frac{f-f'}{f}\cdot\frac{100}{P}\cdot\frac{M}{M_1} = \frac{d_1}{d} \text{ or } \frac{K}{M_1} = 0{\cdot}01\ \frac{d_1}{d},$$

where d_1 is the observed density in the saturated vapour and d that calculated from M_1.

Although by this plan Raoult obtained absolute identity with the expression derived from the theory of solutions, he preferred to regard his formula, founded on fact, as an equation essential to the osmotic law, osmotic pressure still being a value unsuited for direct estimation. This Raoult had learned by a preliminary investigation (*Compt. rend.*, 1895, **121**, 187), abandoned when the manometer broke after the highest osmotic pressure ever observed, namely, 50 atmospheres, had been attained, a value far higher than is wanted in these experiments.

We are now coming to the end. Raoult's constitution seems to have been a vigorous one; the only indication to the contrary which I can discover is that in 1887 he resigned an additional professorship of Chemistry and Toxicology at the Grenoble Medical School, which he had held since 1873; this he resigned on account of his health, at first provisionally, and then, in 1892, for good. The 7th of April, 1900, was the date for his official superannuation, but by a special decision of the Board of Trustees, he remained in office, *hors cadre*, a

Grenoble, le 3 Février 1887.

Mon Cher collègue,

J'accepte avec plaisir l'insigne honneur d'être inscrit au nombre de vos collaborateurs au Journal de Physico-Chimie.

Le moment est venu, en effet, d'alléger la Physique et la Chimie, proprement dites, de cette partie commune qui les embarrasse de plus en plus, et d'en constituer une branche spéciale de la science. La publication de votre Journal répondra à un véritable besoin; et, j'en suis convaincu, elle sera saluée avec joie par tous ceux qui, en Europe, s'intéressent aux progrès de la chimie générale.

Permettez moi, Monsieur, en vous envoyant mon adhésion empressée, d'y joindre tous mes remerciments pour l'envoi de votre mémoire sur les lois de l'équilibre Chimique; travail d'une grande puissance et dont l'étude m'emplit d'une véritable admiration.

Veuillez agréer, Mon cher collègue, l'assurance de ma haute estime et de mon entier dévouement.

Raoult

Professeur de Chimie à la faculté des Sciences de Grenoble.

very high distinction and a proof of his unbroken vigour at that time. Yet, wise man as he was, he used well those days, no doubt fearing that they might not last, and in two exhaustive treatises, dated 1900 and 1901, he published his final views on Tonometry and Cryoscopy (*Scientia*, No. 8 and No. 13); it was just in time, for, without any warning symptoms, he died, almost suddenly, on April 1st, 1901.

As I had not the honour of being personally acquainted with Raoult and only occasionally corresponded with him, I must rely on the verdict of others if I venture to consider him as a man. Yet his character may be read in his papers: activity, patience, tenacity to an extreme degree in pursuing an aim, having an eye as much for detail as for vaster and vaster horizons, absolute independence of mind, power of criticising or of admitting without passion the views of others as well as his own, and of testing both with the same calm conviction that the last word must rest with experiment; this is what we read in every page and what the whole chemical world may know.

Looking at him still more closely, let us read what was said in the name of the University and of the Faculty at the grave in that Grenoble which Raoult had chosen for his residence during more than thirty years. Possessor of the highest local distinctions, if such may be counted; *doyen*; holder of the only medal of the French Government for services given by him as vice-president of the *Conseil d'hygiène de l'Isère*, the representative man of the University: words fail me to express how greatly he was regretted both on account of his character, and of the distinction which he had conferred on the city which mourned him.

To her who best must have known Raoult I am indebted for my last and best words*:

"'Ce que fut l'homme privé, tous ceux qui l'ont connu ont apprécié cet esprit bienveillant, fin, spirituel, cette extrême bonté, cette modestie à toute épreuve.

'Il ne m'appartient pas de vous dire ce qu'il fut pour les siens, se dévouant à eux entièrement, les entourant de son amour, de sa sollicitude.

'Tendre père, il eut l'immense douleur de se voir enlever une enfant de 8 ans, et plus tard une fille de 26 ans, laissant un enfant à qui il prodigua toutes ses tendresses.

'Puisse ce rècit bien douloureux pour moi vous faire comprendre que comme homme et comme savant celui que je pleure mérite tous les regrets.'"

* Letter from Mme. Raoult, Grenoble, January 24th, 1902.

Johannes Wislicenus

WISLICENUS MEMORIAL LECTURE.[1]

By W. H. Perkin, jun.

When Johannes Wislicenus passed away, two years ago, an acute sense of loss was felt, not only in the world of Science, where his name had long been placed among those of the great organic chemists, but also in other fields where men of science have but seldom left deep impressions of their personal influence.

Innate qualities, obscured as they so often may be by others adventitious or assumed, are not always easy to trace unless history gives the clues. But the character of Wislicenus was even higher than his scientific work, and I am tempted to dwell upon it, rather than on the achievements which are familiar to chemists, because the simplicity and personal force of the man were known to comparatively few, while his chemical fame was, of course, world-wide.

During the seventeenth century, a family of Poles, victims of the intolerant spirit and religious persecution of the time, wandered homeless into Germany, and finding at last congenial surroundings in Schönburg, where for many generations afterwards the family made their home, they took up priestly duties and devoted their lives to the welfare of their fellow-men. Among their descendants was Gustav Adolf Wislicenus, a man who sustained the family traditions and shone with all the fine qualities of his race. The story of his life reveals the fearlessness of his character, and aids us in forming a true conception of the forces in the composition of his son Johannes, for between the two men there was more in common than is usual between father and son.

Gustav Adolf Wislicenus felt the weight of religious oppression at an early age, for whilst yet a student he was condemned to imprisonment on account of his connection with certain sectarian societies. This was in 1824, and it was not until 1829, five years later, that his friends were able to obtain for him a formal pardon and the remission of the remainder of his sentence. After his release he chose the vocation of a Lutheran priest, and from 1834 pursued this calling at the little village of Klein-Eichstädt, near Querfurt, until he was preferred to the Neumarkt-Kirche at Halle in the year 1841.

This period in Prussia was marked by the rapid growth of popular antagonism to the efforts made by the more powerful of the clergy to regulate the form of religious worship throughout the country, and

[1] The author wishes to acknowledge the very valuable assistance which he received from Dr. A. Lapworth while compiling this Memorial Lecture.

this feeling first reached its climax in Saxony, and in particular among the rationalistic clergy. With these pastor Wislicenus threw in his lot. At the great meeting of "Lichtfreunde" at Cöthen in 1844, he gave full expression to his revolutionary views on the foundations of faith, the result being that the supporters of the new ideas found themselves denounced as traitors and their meetings proscribed, Wislicenus himself being expelled from his office two years later.

The growth of the spirit of independence had led to the formation in different parts of the country of a number of 'free congregations,' and the foundation of one of these at Halle was the first object which Wislicenus set himself to attain after his loss of position. Political movement culminated in the revolution of 1848 and the Frankfort Parliament. In the latter, which was a Parliament without statesmen, we find Gustav Wislicenus and many other leaders in the free religious movement occupying positions of prominence and playing active parts.

At this time Johannes Wislicenus was about fifteen years of age. He was born at Klein-Eichstädt on June 24, 1835, the year following his father's appointment at that place, and, when Halle became the home of the family, was sent to the Realschule der Frankeschen Stiftungen, where his marked zeal was followed by well deserved success. He was one of a numerous family whom the expulsion of the father from office threw into dire distress, and the boy's experience of some of the bitter hardships of life helped to steel his youthful frame. Even in these early days he took first place among his comrades and excelled in swimming and gymnastics, but above all in his favourite study, the German language.

Science early attracted his special regard, and on passing from school to the university he soon found himself able to pay her the single-hearted devotion she claims. With his appointment as assistant to Professor Heintz in 1853, he finally dedicated himself to chemistry.

His absorbing chemical studies, so auspiciously begun, were not long to be continued without interruption. The family prospects were clouding over, and in this same year the father was condemned to two years' imprisonment as a consequence of the publication of his work "Die Bibel im Lichte der Bildung unserer Zeit." This new disaster left flight the only chance, and, with the help of trusty friends, Gustav succeeded in making his escape, while the family, under the charge of the young Johannes, followed him.

Proceeding first to England, they embarked for the United States. Ill fortune again overtook them, for the vessel in which they set sail was soon discovered to be cholera-stricken. The ship's doctor found his time and energies fully occupied in attending to the first-class

passengers, and, in characteristic manner, it was young Wislicenus who, in this emergency, acted as physician and nurse to the forsaken occupants of the steerage. When all hope of stamping out the scourge at last disappeared, the ship put back to England, where the family lived in straitened circumstances until they were again able to set out for the New World.

The sojourn in America was not of long duration, for at the end of two years they found it possible to return to Europe. During this time the scientific knowledge of Johannes was the means of support on which the family relied, and he was fortunate enough to obtain an appointment as an assistant to Professor Horsford, of Harvard, and afterwards he conducted an analytical laboratory of his own in New York.

Zürich became the headquarters of the family on their return to Europe. The son was able to resume his interrupted scientific career at Halle, under Heintz, whom he rejoined in 1857, and with whom he remained until the autumn of 1859.

The friendship which sprung up between the two chemists lasted until the death of Heintz, twenty years later. Their association was marked by the publication of several joint researches. One of these dealt with a base they isolated from the products obtained by heating aldehyde-ammonia on the water-bath, to which, in the symbols then in use, they assigned the formula $C_{16}H_{13}NO_2$.[1] The compound is that now known as "oxytetraldin," $C_8H_{13}NO$.

A second communication dealt with experiments on goose-gall and the nature of some of its complicated acidic constituents.[2] A third one, of more general interest, resulted in the disappearance from literature of the "aldehydic acid" which Liebig considered was an intermediate step in the oxidation of acetaldehyde to acetic acid. The paper by Heintz and Wislicenus[3] exposed the slender character of Liebig's evidence, and indicated that acetic acid is the only definite product obtained when acetaldehyde is treated with silver oxide in accordance with Liebig's directions.

It was at this time also that the first papers by Wislicenus himself appeared.[4] These dealt with his own views as to the relationship of glycol and glycerine in the light of the type theory which was then the guiding principle of classification.

In 1859 Wislicenus left Halle for Zürich. This step was his reply to the action of the governing body of the Halle Hochschule, who, before allowing him the title of 'Privatdocent,' required him to offer

[1] *Poggendorff's Annalen*, 1858, **105**, 577.
[2] *Ibid.*, 1859, **108**, 547.
[3] *Ibid.*, 101.
[4] Halle, *Zeit. Gesammt. Naturw.*, 1859, **13**, 270, 442; **14**, 97; *J. pr. Chem.*, 1859, **77**, 149.

guarantees that he would in future refrain from all public expression of his political opinions. Such an attempt to bring pressure on him was foredoomed to failure. His principles, absorbed first from his father and afterwards from his friends in freedom-loving America, were already firmly fixed; he had come to regard the enunciation of his political and religious principles as part of his life's work, and throughout his career he was ever active in their furtherance.

At Zürich his progress was rapid. He was appointed Professor of Chemistry and Mineralogy, under the Council of the Canton, at the School of Industries, in 1861. Three years later he was made Extraordinary Professor and Director of the Laboratories in the University, and in 1867 Ordinary Professor. In 1870 the Education Council conferred on him the Chair of Chemistry in the Polytechnic, and a year later he was made Director.

In Zürich the problems connected with his investigation of the lactic acids absorbed his special interest. The question of the most suitable formula for the acid, which Scheele had discovered in the eighteenth century, was engaging much attention among chemists and provoking interesting controversy. On some points a preliminary agreement seems to have been attained, but it was generally recognised that searching experimental study was necessary if a final verdict was to be pronounced. The natural development of his earlier research work led Wislicenus to examine the points at issue, and he soon perceived that, to a certain extent, the facts as then known were in harmony with prevailing theories of structure, but that much was left without explanation, and appeared to call for some modification or extension of the existing views.

According to the conceptions of structure in use at that time, two, and only two, isomeric lactic acids should be capable of existence, and these should be characterised by complete disparity in properties. Wislicenus had isolated from meat-extract a lactic acid which was not identical with Scheele's well-known substance, but the difference was not so marked as was to be anticipated in the case of an isomeride such as the theory predicted. The effort to ascertain, by synthetic methods, the constitution of the two acids proved exceedingly difficult, the products being mixtures of several substances of which ordinary lactic acid certainly appeared to be the main constituent. Finally, a third distinct compound having the composition of a lactic acid was discovered by Beilstein; in regard to this latter substance, however, its recognition as a third isomeride was greatly delayed by an unfortunate mistake on the part of its discoverer. The discovery, in fact, increased instead of simplifying the complexity of the question.

At the present time, having the key in our possession, we are able to trace without difficulty the structural relationship of these acids

which, to those workers, was obscured by masses of detail. These details are now of secondary importance. They serve, however, to make clear to us the way in which the first suspicions in the mind of Wislicenus were aroused.

Even when surmise became conviction, it would not have been characteristic of his judicial intellect had he altogether discarded the theories which he perceived to be in the main so fruitful and so nearly accurate. To him it was more natural to assume that the explanation might be found in some extension of these theories, and with brilliant discernment he showed the precise direction in which that extension was to be made, namely, by taking into account the arrangement of the various parts of the molecule in tridimensional space, and he even attempted to represent such a conception in a graphic manner.

His views were expressed in his address to the Naturforscherversammlung at Innsbruck in 1869, and shortly afterwards he gave them a wider publicity in the new *Berichte der deutschen chemischen Gesellchaft*[1] in connection with a paper on the modifications of lactic acid. The precise words he employed are worthy of quotation. "Tatsachen wie diese werden dazu zwingen die Verschiedenheit isomerer Molecüle von gleicher Structurformel durch verschiedene Lagerung ihrer Atome in Raum zu erklaren und sich nach bestimmten Vorstellungen daruber umzusehen."

The new shoot which was thus grafted on the stock of structural chemistry did not at once show signs of growth, although it was imperceptibly acquiring vitality as the external conditions were becoming more suited to its free development.

It was at Zürich, also, that Wislicenus interested himself for a time in the question of the origin of muscular energy, his association with his friend and colleague Adolf Fick being doubtless responsible for his temporary divergence in this direction.

At that time Liebig's theory held the field, it being generally supposed that the energy necessary for muscular power was furnished by the combustion of the muscle-substances, that is to say, of nitrogenous albuminous materials, whilst that supplied by the oxidation of the carbohydrates and fats was mainly of use in maintaining the temperature of the body. This theory did not commend itself to Fick and Wislicenus, and on August 30, 1865, they undertook the ascent of the Faulhorn, near Interlaken, for the purpose of obtaining direct experimental evidence on the point. The minimum work done in the ascent was easily calculated, whilst the amount of nitrogen in the urine voided during the journey supplied the basis for computing that part of expended energy which was supplied by the destruction of the muscle-material, a computation which subsequent experiments

[1] 1869, **2**, 620.

of Frankland rendered even more simple. The results indicated that the nitrogenous constituents were responsible only for a certain part of the energy expended, and the later investigations of Voit, Pettenkofer, and others have entirely confirmed this conclusion.

In 1872 Wislicenus was invited to succeed Adolf Strecker at Würzburg, and the move must have been congenial to him, for it brought him closely into contact with a number of men of intellect, including Kohlrausch, von Wagner, Sachs, and Sandberger. Here his attention turned more particularly to problems of a nature suited to the powers of the numerous young workers whose studies he was called on to direct. From his fertile imagination fell the ideas which were the starting points of many fruitful and varied experimental investigations. In particular, the syntheses with the aid of molecular silver, and those involving the use of acetoacetic or malonic ester, led to the development of fields in which his students found abundant space for useful work. The extraordinary volume and the importance of the new observations which flowed from his laboratories during this period evoked the admiration of the scientific world.

The time and attention which his synthetic researches claimed left Wislicenus few opportunities for other investigations, and the development of the conception of space configuration and its influence on isomerism was making but little progress, at least on the practical side. In the interval, however, the theoretical foundation on which is based our present view of stereochemical relationships among carbon compounds had been laid by van't Hoff and Le Bel. "La Chemie dans l'Espace," van't Hoff's famous thesis, appeared in 1875, and it is not to be doubted that Wislicenus, perhaps more clearly than any other chemist, foresaw at once the vast fields of research which the new theory was to open up. At his desire, a German edition of van't Hoff's work was undertaken by Felix Hermann. This appeared in 1877 under the title "Die Lagerung der Atome im Raume," and contained the matter of the French edition together with a preface by Wislicenus himself, who did not rest with this effort to make the new hypothesis familiar to a wide circle, but took every available opportunity to press its merits on the chemical world, which was disposed to accord it a cold reception, and, in some quarters, even to greet it with derision.

The death of Kolbe, the most uncompromising opponent of "chemistry in space," left vacant the Chair of Chemistry at Leipzig, and the University was set the difficult task of finding the man most fitted to take his place. The great, and perhaps not unexpected, honour fell to Wislicenus, and in 1885 he entered on his new duties, which he continued to discharge until his death two years ago.

At Leipzig, Wislicenus was at last able to give his whole mind to

the question of the space distribution of the molecule, the first definite step forward being found in a paper to the Königl. Sächs. Gesellschaft der Wissenschaften in 1887.[1] This paper was entitled "Ueber die räumliche Anordnung der Atome in organischen Moleculen und ihre Bestimmung in geometrischisomeren Verbindungen," and was based on van't Hoff's conception of the analogy between a carbon atom and a regular tetrahedron, but involved considerations of a chemical nature on which van't Hoff had barely touched. The mutual attractive or repulsive forces of the groups attached to adjacent carbon atoms were considered in connection with the relative positions which these atoms, when only singly bound to one another, would be likely to adopt.

The history of his subsequent investigations in this field is so recent and generally so well known that I may leave the details for later discussion, since it is impossible in a few words to convey an adequate impression of the services which they rendered to the science of stereochemistry.

Turning for a while to Wislicenus in the *rôle* of teacher, it may be at once asserted that his claim to our grateful recollection is of the highest. He was endowed with all the qualifications which should form the real basis of a great teacher, and on that foundation he built with scrupulous care, and the words he used in speaking of his old master Heintz applied not less truly to himself: "Wie der Forschertätigkeit, so war ihm auch sein Lehramt und der Umgang mit der Jugend Hertzensache."

Doubtless to the beginner and to young medical students the matter of his lectures must have seemed somewhat tough, but his hearers, one and all, were impressed by his lucidity and by the lively and interesting way in which he presented the material he handled. The feeling that the lecturer was thoroughly at home in all departments of his subject quickly won the confidence of every audience which he addressed.

In the laboratory he was equally conscientious and successful. Everyone there, down to the youngest worker, was personally known to him. By the careful questions he put, he aroused their pride in making accurate observations, and urged them to think and investigate for themselves, thus awakening their interest and developing their skill. He found the way to imbue those who worked under him with something of his own persistence, so that, in spite of experimental difficulties or long series of reverses, they came to regard the abandonment of a piece of work as an idea not to be entertained.

Discussions with his pupils were a source of real pleasure to

[1] Wislicenus gave the substance of this paper in a lecture to Section *B.* at the meeting of the British Association in Manchester in 1887.

Wislicenus, and by founding the Chemical Societies of Zürich, Würzburg, and Leipzig, of which he was always the life and soul, he aimed to bring students and staff more closely into contact, and thus simultaneously to strengthen their desire to acquire a wide knowledge and to increase their interest in research work. It is perhaps not too much to say that the intellectual development of young chemists was to Wislicenus a study as absorbing as any of his chemical problems.

Many of us must recall with pleasure the weekly meetings at which Wislicenus gathered his students round him at his simple mid-day meal. His house was open to students and friends of all ages and positions, and here, as well as at the annual "Bierfrühschoppen," where he entertained his colleagues and pupils, the genial and kindly nature of their host was patent to all.

Those of us who shared these privileges are not likely to forget the impression produced by his personality. His long beard, his fine head with its intellectual features, and his majestic carriage aided in producing a sensation which in younger men was not far from veneration.

The warm feelings entertained towards him by his students doubtless gave him keen pleasure, but formal tokens were always distasteful to him. At the approach of his sixtieth birthday it came to his ears that covert preparations were on foot to give special recognition to the occasion, and the distress which he showed was so evidently sincere that nothing remained but to abandon any idea of celebration.

To his love for teaching may be traced the reappearance of Strecker's text-book, originally based on Regnault's "Premiers Eléments de Chemie." After the death of Strecker in 1871, Wislicenus took upon himself the task of rewriting this book, which involved him in many years' work. In 1874 the organic portion was published (sixth edition), but the inorganic portion (ninth edition) did not make its appearance until 1887; both were in reality new works, for during the years which intervened the condition of chemistry had undergone a complete transformation.

If to the task of carrying on his scientific work and to the guidance of his pupils he devoted most scrupulous care, he was not less punctilious in the fulfilment of other duties which fell in no short measure on his shoulders. Of his professorial functions one of the least agreeable was that of examining, but the irritation which an examination entailed on him did not affect the sincerity of his efforts to form a just estimate of the men who came before him.

His colleagues have borne eloquent testimony that his thorough grasp of detail as well as principle was noticed in all his dealings with the faculty of his University. Seldom was he absent from a business meeting, and it was not often that an important question was mooted on which he had not some illuminating suggestion to make. His

advisory reports were always constructed with great care, and were clear and finished. In addition to the duties of his chair, he found time in Leipzig to fill the offices of Dean and Rector magnificus, positions to which, as was generally conceded, he brought exceptional dignity. Twice in Würzburg he was honoured by a call to the Rector's seat, and on the second occasion the summons implied more than ordinary confidence in the man selected, for the tenure of office was intended to cover the celebrations in commemoration of the 300th year of the University's existence.

In spite of the extraordinary calls which his acadamic and scientific work made on his energy, he still was able to take a prominent part in political affairs. So far as was possible, he held himself aloof from party strife, and for this reason he staunchly resisted all proposals that he should submit himself for election to the Reichstag, and only consented with reluctance to take office as a town-councillor at Leipzig. But when the call came to fight for large ideals and for the future of the German people, the instincts of the leader always brought him to the front.

Wislicenus was a German to the core. At school the German language was one of his hobbies, and the folk-lore and mythology of his country were an absorbing study. His long exile in other lands only served to strengthen his patriotism, and he followed heart and soul the efforts of his countrymen to form a united nation. He was an ardent follower of Bismarck, and never hesitated to give the freest expression to his opinions. He strove constantly to promote a German colonial policy, and was a keen advocate of proposals to form a great German navy. Nevertheless throughout his life he kept a warm place in his heart for Switzerland, his foster-mother.

An incident which illustrates some of the prominent features in the character of Wislicenus may be related. Shortly after the conclusion of peace between France and Germany, a gathering of the German inhabitants of Zürich was held to celebrate the occasion, and Wislicenus was nominated chairman. The Francophile portion of the population attacked the meeting hall with stones, and set fire to the staircase. A panic arose among the merry-makers, but Wislicenus, with a well-timed appeal to their patriotism, restored their confidence, and then proceeded, with the utmost coolness, to show them how defences might be formed, and to extinguish the burning stairs with beer.

He left the hall immediately afterwards, and walked quietly through the mass of excited people whose intention it had been to stone him. But his commanding presence at once put a stop to any such idea, and no one ventured to assault him.

Shortly after he settled in Zürich, Wislicenus married Katherine

Sattler, the grand-daughter of Wilhelm Sattler, of Schweinfurt, wh shared with Russ the discovery of "Schweinfurt green." His happiness was not long unmarred by misfortune, for in 1866, Hugo, his brother, who at the time was Privat-docent in the Faculty of Germanic Archæology at Zürich, lost his life as the result of an accident in the Alps. This blow was followed by others even more severe. His wife, after ten cloudless years, was seized with an incurable mental disorder, and two gifted sons were taken from him before attaining manhood. The marks made by these calamities were never effaced, but the interest which he took in his fellow men was not thereby lessened. He sought to save his friends distress by striving to conceal his pain, and it is more than likely that the restraint which he thus imposed on himself started the first tremor which finally led to the breakdown of his overburdened frame.

His two remaining sons followed in their father's footsteps, and he was able to rejoice in their successes. Of his two daughters, the elder, Emilie, remained with him until his death, sharing his joys and troubles; his second daughter, Marie, lived in Zürich after her marriage, and in later years father and daughters met there at frequent intervals. The relations between Wislicenus and his children were ideal, and the sympathy which bound the household can fully be realised only by those who have had the privilege of entering the family circle. Holidays, to them, meant the fields and woods. The father had built a charming country house in the Schonungen district, not far from Schweinfurt, and there, in the peaceful valley below the picturesque fortress of Mainberg, he spent a part of his vacations in quiet study, or sought to gain new energy by tramping the woods with gun on shoulder and his mind full of the interests of country life.

I may now be permitted to review in greater detail some of the scientific work associated with the name of Johannes Wislicenus. At the commencement of his career, the study of organic chemistry had greatly weakened the hold of the Berzelius dualistic electrochemical theory, at least as a universal principle, for the direct application of that conception to carbon compounds had proved fruitless, and it was beginning to be felt that even the "radical" theory of Liebig and Dumas would prove inadequate. A brilliant procession of new and unexpected observations was passing before the eyes of the chemical world, and the revolutionary ideas of Gerhardt were attracting the fancies of the younger schools of chemists, although, as is usually the case when doctrines of tried utility are threatened by overthrow, the new views were opposed by several of the elder men.

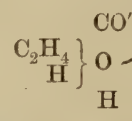
It was entirely in accordance with the independence of thought which his judgment so often displayed that, in his first contribution to chemical literature, of which mention has already been made, Wislicenus dissociated himself from the conservatism of his teacher, Heintz, and proclaimed himself an adherent of the new principles. Simultaneously with this theoretical paper on glycerine and the polyatomic alcohols appeared others in which was detailed the experimental basis for the conclusions drawn, the principle that theory and experiment must yield each other mutual support being his guide throughout his scientific career.

When Wislicenus resumed work at Zürich, the problem of the constitution of lactic acid was in the air. The discovery of glycol by Würtz in 1856, and the publication of Heintz's synthesis of glycollic acid from chloracetic acid, had paved the way for a preliminary agreement between the schools of Würtz and Kolbe. The former saw in lactic acid a "diatomic radical, $C_3H_4O_3$"; the latter based his views on the broader conception that the substance was really a monobasic acid, and endeavoured to show that it was very simply derived from propionic acid, which he conceived as "ethyl formic" acid; to lactic acid he, therefore, attributed the functions of a "(hydr)oxyethyl formic" acid, and, in the older symbols to which he permanently adhered, he expressed its structure by the type formula $HO\left(C\left\{\begin{matrix}H\\HO_2\end{matrix}\right.\right)[C_2O_2],O.$

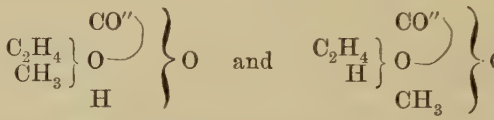
Wislicenus entered the field without preformed notions, and, recognising that the difference of opinion arose largely as the result of too narrow conceptions of the type theory, endeavoured to show that it was easy, merely by extending the idea of radicles within radicles, to express all that was then known as to the behaviour of lactic acid. He emphasised the fact that, in accordance with Kolbe's view, lactic acid is monobasic, and that the *second* replaceable hydrogen atom has the same character as the replaceable hydrogen in alcohols.[1] The *di*sodium derivative of lactic acid behaves in much the same manner as does an alcoholate, being decomposed by carbon dioxide, and even by water, into the *mono*sodium derivative and sodium carbonate or hydroxide, whilst the formation of a sodium derivative of ethyl lactate is in accordance with the belief that this ester still retains an alcoholic function. He considered, in the terms then in vogue, that the divalent carbonyl radicle is "neutralised" on one side by union with a positive, univalent alcohol radicle, leaving it negatively univalent, whilst in the alcohol radicle itself there is also the hydrogen atom, which is replaceable by acid groups and capable of being removed with the oxygen atom in exchange for an atom of chlorine.

[1] *Annalen*, 1863, **125**, 41—70.

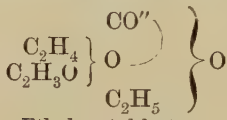
The formula he employed to crystallise his view of lactic acid was



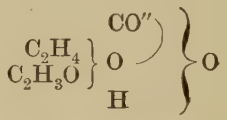
and he indicated how clearly this accounted for the isomerism of the two methyl derivatives:



and by hydrolysing Perkin's ethyl acetyl-lactate he succeeded in isolating acetyl-lactic acid and its salts:



Ethyl acetyl-lactate.



Acetyl-lactic acid.

He went on, shortly after this, to the study of malic, tartaric, citric, and mucic acids,[1] to which similar views appeared to be capable of application. These acids were generally recognised to be dibasic in character, and Kekulé regarded malic acid, for example, as a "triatomic dibasic" acid, whilst Kolbe preferred to picture it as a "dibasic mono(hydr)oxy" acid. In order to determine how far the additional oxygen atoms in these acids correspond in function with the third oxygen atom in lactic acid, Wislicenus investigated the action of acetyl chloride on their neutral esters, the conclusions which he was able to draw being, (1) that the so-called atomicity of an acid is the sum of the positive hydrogen atoms which are easily replaceable by metals or alcohol radicles and of the negative hydrogen atoms which are replaceable by acid radicles; (2) that the number of the negative hydrogen atoms of the second type is best determined by the action of acetyl chloride on the neutral esters.

While dealing with his conception of the univalent radicle $\left.\begin{matrix}C_2H_4\\H\end{matrix}\right\}'O$ in his lactic acid formula, he pointed out that such a radicle is existent in glycolmonochlorhydrin, $\left.\begin{matrix}\left.\begin{matrix}C_2H_4\\H\end{matrix}\right\}'O\\Cl\end{matrix}\right\}$, and other glycol compounds.[2] He endeavoured to replace the halogen atom in glycolmonochlorhydrin by the cyano-group through the agency of potassium cyanide, and by hydrolysis of the product to convert the compound

[1] *Annalen*, 1864, **129**, 175—200. [2] *Ibid.*, 1867, **128**, 1—67.

into one of the carboxylic type. The method afforded him an acid having the formula $C_3H_6O_3$, which at the time he considered in all probability to be paralactic acid (now known as α-hydroxypropionic acid), trusting to observations on the properties of its zinc salt for the evidence as to its identity. It must be said, however, that subsequent experiments of Erlenmeyer[1] proved that the conclusion drawn by Wislicenus was erroneous, for the acid obtained from glycolchlorhydrin by the above mode of treatment yields the characteristic zinc-calcium salt of hydracrylic acid (or β-hydroxypropionic acid); Erlenmeyer also showed that this method gives but a poor yield of the synthetic product, which is more easily obtained if the intermediate ethylene cyanohydrin be prepared by leaving together a mixture of ethylene oxide and hydrocyanic acid.

The existence of a genetic relationship between acetaldehyde and lactic acid proper had been rendered probable by Staedler and by Engelhardt among others, for aldehyde could be obtained from the acid in several different ways; Strecker, moreover, had effected a synthesis of lactic acid from acetaldehyde by way of alanine (α-aminopropionic acid). These facts suggested to Wislicenus that the divalent radicle, C_2H_4'', of ordinary lactic acid was identical with the "ethylidene" radicle of acetaldehyde, and he confirmed this suggestion experimentally by a synthesis of lactic acid from the aldehyde—a synthesis which was analogous, at least in appearance, to that by means of which glycolchlorhydrin had yielded him the isomeric acid. The process consisted in preparing the requisite ethylidenechlorhydrin by the direct addition of hydrogen chloride to aldehyde, and subjecting the halogen compound to the usual processes; he also effected the synthesis by the now well-known method involving the formation of ethylidenecyanohydrin by direct addition of hydrogen cyanide to the aldehyde.

At this juncture he considered the results of experiments to justify the conclusion that the existence of two isomeric C_2H_4'' radicles in paralactic acid from meat juice and ordinary lactic acid respectively was established; in the paper appear for the first time the names "ethylenelactic acid" and "ethylidenelactic acid," and these terms have remained in common use up to the present time, although the error made by Wislicenus in the application of the former term to paralactic acid was soon corrected when Erlenmeyer showed that hydracrylic acid was the compound to which it should properly be assigned.

In the same paper which contains the account of these results[2] is to be found an interesting discussion on different modes in which the reactions of lactic acid could be expressed by type-theory formulæ, and a free translation of the concluding remarks on this subject may be

[1] *Annalen*, 1867, **141**, 261. [2] *Ibid.*, 1863, **128**, 1 *et seq.*

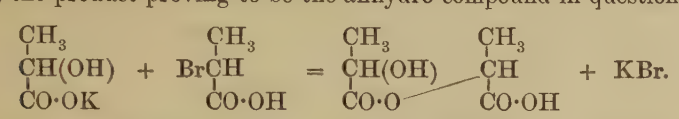
given. "The formulæ for lactic acid, which I have given above, represent, not different, but one and the same kind of combination between the parts of the lactic acid molecule; the radicles in them are identical, the kind of mutual saturation is the same throughout, and the only change made is the order in which they come. Such a change in order would always be justified even if we understood the mode in which the atoms are distributed in space, because our present formulæ can do no more than present us with a picture of the compound in one plane. If we wish to represent the properties of a compound from all points of view, many different formulæ, emphasising different characteristics, are necessary, and so long as these different chemical formulæ exhibit the differences in order only and not in the type of union of the adjacent parts, so long, in my opinion, will they be wanting in scientific precision." He here seized the opportunity to point out that the theory of molecular structure must be set on a broader basis, remarking that it was no longer possible to contend that the equivalent substitution of hydrogen produces only secondary effects on the general character of a compound.

The properties of the so-called "anhydrous lactic acid" next absorbed his energies.[1] Pelouze had investigated the action of ammonia on this substance, and found that ammonium lactate was formed, whilst Laurent found that only one-half of the ammonia absorbed could again be directly obtained in the form of platinichloride, the other half being combined in a non-separable form. Laurent drew the conclusion that the product he obtained arose as the result of a decomposition of an ammonium aminolactate or lactamate, Wislicenus[2] had already suggested that "anhydrous lactic acid" was ester-like in character, one residue of lactic acid functionating as the acid radicle and another as the alcoholic radicle, so that by the action of ammonia it might be expected to afford one molecule of lactamide and another of lactic acid, or rather of its ammonium salt; by carrying out the reaction with ammonia in an alcoholic solution of "anhydrous lactic acid," he was able to prove that both these compounds are formed immediately, and therefore are not merely secondary products as Laurent had supposed.

During the next two or three years a great advance was made, because Frankland's graphic methods of representing the constitution of carbon compounds began generally to be adopted, and we find them employed in all the subsequent communications from Wislicenus on the subject of lactic acid, hence it will not be inconsistent if at this point I follow the sequence of historical events, and at once employ the modern graphic symbols to depict the process by which Brügger, in 1864, confirmed the views of

[1] *Annalen*, 1865, **133**, 257. [2] *Ibid.*, 1863, **128**, 60.

Wislicenus regarding the nature of "anhydrous lactic acid," or "dihydrolactic acid," as it has more recently been termed. Brügger's method [1] consisted in heating potassium lactate with α-bromopropionic acid, the product proving to be the anhydro-compound in question.



A striking observation of Strecker's arrested the attention of Wislicenus; by the action of heat on sarcolactic acid, an anhydride of ordinary lactic acid was obtained, and Wislicenus, who at this time considered that sarcolactic or paralactic acid was ethylenelactic acid, supposed that this involved a conversion of β-hydroxypropionic acid into α-hydroxypropionic acid, and in order to determine if such a change might be brought about in the homologues of lactic acid, he examined the properties of the hydroxybutyric acid which he prepared for the purpose by the reduction of Geuther's acetylacetic ether. This acid he considered to be the analogue of paralactic acid, for the isomeric acid prepared by Friedel and Machucca from brominated butyric acid he correctly supposed to be the corresponding α-hydroxy-acid. He was unable to satisfy himself that, on heating β-hydroxybutyric acid, any change took place corresponding with that noticed by Strecker in the case of paralactic acid, but observing that the salts of β-hydroxybutyric acid swelled when heated, he suggested that the non-occurrence of the expected isomeric change was the result of the conversion of the compound into the unsaturated acid by loss of a molecule of water.[2] It is now clear, of course, that the change which paralactic acid undergoes when heated is a simple case of racemisation, such as occurs also in the case of mandelic acid, involving no further structural alteration.

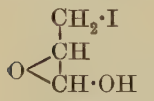
It was at about this time that his first important paper on the acid from β-iodopropionic acid made its appearance.[3] Beilstein had previously carried out the hydrolysis of the iodo-acid by moist silver oxide, but, unfortunately, had failed to recognise the true character of the product, to which he assigned the name "hydracrylic acid" and the formula $C_{12}H_{22}O_{11}$. Two years afterwards, Moldenhauer found that Beilstein's acid could be converted into a compound having the same empirical formula as lactic acid by heating it with a solution of alkaline hydroxides, and this paper was succeeded by others emanating from Wichelhaus and from von Richter. Wislicenus re-examined Beilstein's acid, and, by preparing its crystalline salts, succeeded in proving that

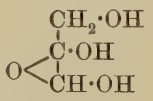
[1] *Zeit. für Chem.*, 1869, **5**, 338.
[2] *Annalen*, 1869, **149**, 205—215.
[3] *Zeit. für Chem.*, 1868, **4**, 683—684.

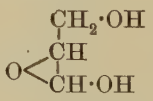
it was isomeric with lactic acid. He returned to the subject some years later[1] in consequence of an expression of opinion from Wichelhaus, who considered that hydracrylic acid was identical with ethylenelactic acid; an opinion which Wislicenus did not share, although, as he believed, ethylenelactic acid is undoubtedly present in small quantities in the crude acid from meat-extract. It is only fair to note that both Erlenmeyer and Klimenko failed to confirm the latter statement. Wislicenus showed that the action of silver oxide on β-iodopropionic acid affords, not only a lactic acid, but also acrylic acid, $C_3H_4O_2$, and two isomeric acids having the formula $C_6H_{10}O_5$. which he termed dehydracrylic and paradipimalic acids respectively, Heintz, by warming β-iodopropionic acid with milk of lime, also observed the formation of lactic and acrylic acids, but did not detect the other acids discovered by Wislicenus; he also discovered the characteristic double zinc-calcium salt of the lactic acid formed. Heintz, like Wichelhaus, believed that Beilstein's acid must be regarded as ethylenelactic acid.

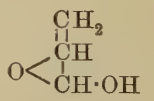
The reason urged by Wislicenus in support of his contention that hydracrylic acid is not ethylenelatic acid was that he was unable to convert it into malonic acid, which the latter afforded him without difficulty; moreover, the acid which he had obtained from ethylene-chlorohydrin had refused to yield β-iodopropionic acid on treatment with hydrogen iodide, and gave only amorphous salts, whilst hydracrylic acid could be reconverted into β-iodopropionic acid without difficulty.

He considered that the two compounds were very closely related, however, and suggested that β-iodopropionic, glyceric, hydracrylic and acrylic acids were not true carboxylic acids, and his conception of their relationship was expressed by the following formulæ :—


β-Iodopropionic acid.


Glyceric acid.


Hydracrylic acid.


Acrylic acid.

It was the experiments of Erlenmeyer,[2] to which reference has already been made, which revealed the trap into which Wislicenus had fallen, and served to establish the identity of hydracrylic and ethylenelactic acids.

Wislicenus, in 1873, once more took up the investigation of the acids from meat-extract,[3] and confirmed Strecker's observation that paralactic acid may be converted into the anhydride of ordinary lactic acid,

[1] *Annalen*, 1873, **166**, 3, *et seq.* [2] *Ibid.*, 1878, **191**, 261.
[3] *Ibid.*, 1873, **166**, 3—64; **167**, 302—346.

and proved that, by heating the former at 135—140°, a complete conversion of the active into the inactive acid may be brought about. Comparative experiments on the two acids showed him that both compounds yield aldehyde and under precisely similar conditions, forcing him to the conclusion that there is no profound difference in structure between the two, so that the facts accumulated up to that time indicated clearly enough that paralactic acid and fermentation lactic acid must be represented by the same chemical formula,

$$\begin{array}{l} CH_3 \\ | \\ CH\cdot OH. \\ | \\ CO_2H \end{array}$$

It is worth while to quote the words in which he announced his conclusion to the German Chemical Society,[1] for they must be memorable as marking the first step towards the development of chemistry in space. "Es ist damit der erste sicher constatierte Fall gegeben, dass die Zahl der Isomeren die der Struckturmöglichkeiten übersteigen kann. Tatsachen wie diese werden dazu zwingen, die Verschiedenheit isomerer Molecüle von gleicher Struckturformel durch verschiedene Lagerung ihrer Atome im Raum zu erklären und sich nach bestimmten Vorstellungen darüber umzusehen."

For the type of isomerism which depends on the varying space distribution of the atoms in the molecule, he used the term "geometrical isomerism,"[2] a name which was afterwards replaced in 1888 by the word "stereoisomerism," coined by Victor Meyer.

The years over which the investigations on lactic acid extended were not without results in other fields. At one time Wislicenus seems to have taken some interest in inorganic chemistry and in water and gas analysis, but this was in his earlier years, and his later work lay almost exclusively in the domain of carbon chemistry.

In 1869 appeared his first paper on the subject of the dibasic acids of the oxalic series $C_nH_{2n}(CO_2H)_2$.[3] The nomenclature which he here proposed for the first few members of the series is practically the same as that in use at the present time, except that "lipic acid" has become "glutaric acid." In this communication the use of "molecular silver" as a synthetic agent is described for the first time; this agent, prepared by the reduction of silver chloride in the cold, was heated with β-iodopropionic acid, first at 100—120°, and then at 150—160°, the product being adipic acid,

$$2CO_2H\cdot CH_2\cdot CH_2\cdot I + 2Ag = \begin{array}{l} CH_2\cdot CH_2\cdot CO_2H \\ | \\ CH_2\cdot CH_2\cdot CO_2H \end{array} + 2AgI.$$

[1] *Ber.*, 1869, **2**, 620.
[2] *Annalen*, 1873, **167**, 345.
[3] *Ibid.*, 1869, **149**, 215—224.

A synthesis of another member of this series, namely, succinic acid, was also accomplished, and this experiment appears to have given rise to the long and valuable series of researches on acetoacetic ester which emanated from the laboratories of Zürich and Würzburg under the auspices of Wislicenus. The synthesis referred to consisted in bringing ethyl chloroacetate into reaction with the product obtained by the action of sodium on ethyl acetate—a product which was generally held to be a simple substitution derivative, although Geuther himself maintained the view which is now known to be the correct one. The conception which, at the time, Wislicenus formed of the process was as follows :—

$$Cl\cdot CH_2\cdot CO_2\cdot C_2H_5 + Na\cdot CH_2\cdot CO_2\cdot C_2H_5 = \begin{matrix} CH_2\cdot CO_2\cdot C_2H_5 \\ | \\ CH_2\cdot CO_2\cdot C_2H_5 \end{matrix} + NaCl.$$

The method was found to lead to the formation of a by-product, the investigation of which Wislicenus left in the hands of his pupil Noeldecke, who succeeded in proving it to be acetopropionic acid, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$; this substance, as was afterwards shown, is produced by the elimination of carbon dioxide from acetosuccinic acid, from the ethyl ester of which in reality the succinic acid formed in the reaction is also produced.

In the same year appeared communications on duplothioacetone,[1] which he prepared from acetone by means of phosphorus trisulphide, and on the dibromobenzenes. His investigations on the latter subject were carried out in conjunction with Riese, and included experiments on the action of sodium on the crystalline dibromo-compound, a process which gave rise to diphenyl, diphenylbenzene, and other products ; the oily "β-dibromobenzene" which accompanies the former was purified and converted into its nitro-derivative, and the latter shown to be different from the nitro-compound of crystalline dibromobenzene.

Among the first papers published by Wislicenus after his promotion to Würzburg was a communication on a synthesis of hydantoic acid, which was shown to be the product obtained when cyanic acid acts on glycocoll.[2]

$$\begin{matrix} CH_2\cdot NH_2 \\ | \\ CO_2H \end{matrix} + HCNO = \begin{matrix} CH_2\cdot NH\cdot CO\cdot NH_2 \\ | \\ CO_2H \end{matrix}.$$

The synthesis of ethylmalonic acid from normal butyric acid was accomplished by him in conjunction with Urech,[3] the process involving the conversion of the butyric acid into its α-brominated derivative, which, by the action of potassium cyanide, followed by

[1] *Zeit. für Chem.*, 1869, **5**, 324—326. [2] *Annalen*, 1873, **165**, 103.
[3] *Ibid.* 93—98

the hydrolysis of the resulting α-cyanobutyric acid, gave the substituted malonic acid without difficulty,

$$CH_3\cdot CH_2\cdot CHBr\cdot CO_2H \longrightarrow CH_3\cdot CH_2\cdot CH(CN)\cdot CO_2H \longrightarrow CH_3\cdot CH_2\cdot CH(CO_2H)_2.$$

The years 1874 and 1875 were signalised by the appearance of a long series of communications from the Würzburg laboratories.[1] These were mainly the results of work undertaken by his students, and covered a very wide range. With Goldenberg, benzoin was shown to be capable of reduction to Zinin's desoxybenzoin, and the latter to dibenzyl, while benzoinpinacone was obtained for the first time. Bonné, Goldenberg, and Zimmermann investigated silver derivatives of biuret and its allies, and used them to prepare alkyl derivatives. To Zimmermann was entrusted an interesting piece of work on the constitution of phosphorous acid, the possibility that triethyl phosphite might be represented by the formula $O{:}P\begin{cases}O\cdot C_2H_5\\O\cdot C_2H_5\\O\cdot C_2H_5\end{cases}$ being tested and disposed of by showing that the ester yields no ethylphosphinic acid on hydrolysis, but only phosphorous acid, and that by absorption of oxygen it is converted into ethyl phosphate, $O{:}P\begin{cases}O\cdot C_2H_5\\O\cdot C_2H_5\\O\cdot C_2H_5\end{cases}$; it was also observed that, on addition of sodium hydroxide to concentrated phosphorous acid, a syrup may be obtained in which the ratio P : Na is approximately 1 : 3, the conclusion being drawn that $P(OH)_3$ correctly represents the properties of the acid.

The investigation of the behaviour of zinc ethyl towards dichloroether fell into the hands of Kessel, and Frankland's "dinitroethylic acid" gave Zuckschwerdt results which appeared to Wislicenus to justify the formula $O\begin{cases}N\cdot C_2H_5\\|\\N\cdot C_2H_5\end{cases}$ for that compound. Zuckschwerdt, also re-examined the complex product obtained when sulphur dioxide is brought into contact with zinc ethyl.

A useful synthetic process was worked out by Forster, who found that mercuriphenylammonium chloride reacts smoothly with thiocarbamides, the process leading to the production of guanidines,

$$NHg(C_6H_5)HCl + S{:}C(NHC_6H_5)_2 = HgS + N(C_6H_5){:}C(NH\cdot C_6H_5)_2,HCl.$$

The study of the isomeric solid and liquid crotonic acids was undertaken by V. Hemilian; the pure solid acid gave both "α" and "β" sulpho- and iodobutyric acids, a fact which led Wislicenus to conclude that the formula $CH_3\cdot CH{:}CH\cdot CO_2H$ represented the struc-

[1] *Ber.*, 1874, **7**, 286—298, 683—692, 892—893; 1875, **8**, 1034—1040, 1206—1209.

ture of solid crotonic acid, whilst the liquid acid was presumably $CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$, although, as he admitted, malonic acid is not among the products formed when the liquid acid is fused with potassium hydroxide. This communication is of especial interest when it is remembered that the difference between the two acids was afterwards assigned by Wislicenus to stereochemical causes, the existence of which he was at this time being led to infer from his lactic acid researches.

In the same set of papers is one containing an account of the work which initiated the long series of syntheses by the aid of pure acetoacetic ester which were carried out in the Würzburg laboratories.[1] Wislicenus cited here the new evidence confirming Geuther's views and refuting the suggestions of others that the metal compound obtained by the action of sodium on ethyl acetate is a simple substitution derivative of the latter; the substance was definitely shown to be ethyl *sodio*acetoacetate, and attention was drawn to the improvement in the synthetic process which may be effected if, instead of employing the crude material prepared by heating ethyl acetate with sodium, the pure acetoacetic ester is first isolated; the use of benzene as a diluent and of excess of sodium, afterwards to be removed, was also suggested. Goldenberg, Ehrlich, Zeidler, Saur, and others carried out the experimental details of the work, proving that the product so prepared may afford nearly quantitative yields of substituted acetoacetic esters on treatment with alkyl iodides, benzyl chloride or benzoyl chloride. Finally, it was shown that the *mono*-substituted products are capable once more of reacting with sodium and alkyl iodides, affording the *di*-substituted derivatives, so that the complicated theories put forward by Frankland and Duppa and by Geuther in explanation of the production of dialkylacetic acids, as by-products in the old process, were rendered unnecessary.

With Conrad, whose name afterwards became so closely identified with the progress of the acetoacetic ester and malonic ester syntheses, Wislicenus was able satisfactorily to explain the origin of the dehydracetic acid which is formed by the distillation of acetoacetic ester, four molecules of which interact so that four molecules of ethyl acetate are eliminated,

$$4CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5 = C_8H_8O_4 + 4CH_3{\cdot}CO_2{\cdot}C_2H_5,$$

whilst to Ruegheimer and Harrow is due the joint honour of the discovery of the synthetic reactions by which the sodium derivatives of β-ketonic acids may be converted into diacetylsuccinic esters,

$$2CH_3{\cdot}CO{\cdot}CHNa{\cdot}CO_2{\cdot}C_2H_5 + I_2 = \begin{matrix} CH_3{\cdot}CO{\cdot}CH{\cdot}CO_2{\cdot}C_2H_5 \\ CH_3{\cdot}CO{\cdot}CH{\cdot}CO_2{\cdot}C_2H_5 \end{matrix} + 2NaI.$$

[1] *Ber.*, 1874, **7**, 683.

Other papers published at this period, with Ehrlich, Rohrbeck, Waldschmidt, Saur, Conrad, and others as joint authors, dealt with the continuation of this work. The β-hydroxy-α-substituted butyric acids obtained as reduction products from the alkylacetoacetic esters came under observation, as well as the α-substituted crotonic acids which are produced by their dehydration; thus from methylacetoacetic ester, by this series of changes,

$$CH_3\cdot CO\cdot CH(CH_3)\cdot CO_2\cdot C_2H_5 \longrightarrow CH_3\cdot CH(OH)\cdot CH(CH_3)\cdot CO_2H \longrightarrow CH_3\cdot CH{:}C(CH_3)\cdot CO_2H.$$

a methylcrotonic acid was isolated and identified with the product prepared by Frankland and Duppa from ethomethoxalic acid, $CH_3\cdot CH_2\cdot C(CH_3)(OH)\cdot CO_2H$, by removal of the elements of water. The hydrolysis of methylethylacetoacetic ester yielded a valeric acid which resembled ordinary valeric acid in nearly all particulars, except that its barium salt could not be obtained in a crystalline condition. With reference to this acid the remark is made, "aus dieser Synthese geht mit Sicherheit hervor, dass Erlenmeyer's Vermuthung der sogenannte optisch-active Amyl Alcohol entspreche der Formel $CH_3\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot OH$ und die daraus dargestellte Valeriansäure $CH_3\cdot CH_2\cdot CH(CH_3)\cdot COOH$ in der That richtig sei," a conclusion which, although since proved to be correct, was perhaps scarcely justified by the results of the experiments just mentioned.

Arising out of the study of the action of sodium on ethyl acetate, an examination was made of the compound first isolated by von Fehling as the product of the action of sodium with ethyl succinate. Herrmann was instrumental in proving that the substance is similar in character to ethyl acetoacetate, but yields a mono- and also a di-potassium derivative decomposed by carbon dioxide, the results seeming at that time to indicate that the substance was a ring compound of the formula $\begin{matrix} CH_2\cdot CO\cdot CH\cdot CO_2\cdot C_2H_5 \\ | \\ CH_2\cdot CO\cdot CH\cdot CO_2\cdot C_2H_5 \end{matrix}$.

The investigation of the isomeric ethylacetosuccinic esters Wislicenus assigned to Clowes and Huggenburg; the first of the isomerides was prepared by the interaction of ethyl sodioacetoacetate and ethyl α-bromobutyrate,

$$CHNa(CO\cdot CH_3)\cdot CO_2\cdot C_2H_5 + CHBr(C_2H_5)\cdot CO_2\cdot C_2H_5 = \begin{matrix} CH(CO\cdot CH_3)\cdot CO_2\cdot C_2H_5 \\ | \\ CH(C_2H_5)\cdot CO_2\cdot C_2H_5 \end{matrix} + NaBr,$$

and the second by ethylating acetosuccinic ester,

$$\begin{matrix} CHNa\cdot CO\cdot CH_3 \\ | \\ CH_2\cdot CO_2\cdot C_2H_5 \end{matrix} + C_2H_5I = \begin{matrix} C(C_2H_5)(CO\cdot CH_3)\cdot CO_2\cdot C_2H_5 \\ | \\ CH_2\cdot CO_2\cdot C_2H_5 \end{matrix} + NaI;$$

in accordance with the formulæ assigned, the former was attacked at once by sodium, hydrogen being evolved, whilst the latter was practically unaffected.

The most important communication from the pen of Wislicenus during the year 1877 was, without doubt, a masterly summary of the knowledge which had accumulated up to that time on the subject of ethyl acetoacetate and its applications as a synthetic agent.[1] In the following year this was supplemented by a valuable treatise on the manner in which the proportion of "acid" and "ketone" decompositions is regulated by varied conditions which may be imposed during the hydrolysis of the ester and its substitution derivatives,[2] the remarkable point elicited being the irregular modes in which the esters decompose and the consequent difficulty in foretelling even to a rough degree of approximation the way in which a new ester may behave under given circumstances.

It should be recorded that at about the period of which we are speaking, Conrad and Limpach, pupils of Wislicenus, worked out the details of the method, since then almost universally adopted in carrying out syntheses such as those involving the use of acetoacetic or malonic ester, namely, that of preparing the necessary sodium derivative by a process of double decomposition, the ester being added to alcohol in which the calculated quantity of sodium has previously been dissolved.

The work which Wislicenus entrusted to the author during his stay of two years (1880—1882) in Würzburg was the investigation of the condensation products which are formed when œnanthol is treated with caustic potash or other reagents, a subject which at that time was little understood, but which has since, in the case of other aldehydes, been thoroughly worked out by Lieben and his pupils. But in a laboratory like that of Würzburg, in which so much work of so varied a nature is being carried on, more, perhaps, is learnt by watching others than from the research the student is actually engaged in. The constant contact with men engaged in syntheses with the aid of ethyl sodioacetoacetate and sodiomalonate familiarised the author with these reagents and undoubtedly helped to suggest the methods which were subsequently employed in his researches on the formation of closed carbon chains. Indeed the first small experiment on the action of ethylene dibromide on the sodium compound of ethyl malonate was carried out in the Würzburg laboratories, but at that time without result.

The scientific papers associated with the name of Wislicenus between the years 1877 and 1887 are few in number; one or two dealing with compounds obtained by the acetoacetic ester synthesis, as well as others containing the results of experiments on dichloro-

[1] *Annalen*, 1877, **186**, 161—228. [2] *Ibid.*, 1878, **190**, 257—281.

ether and on reduction products of phthalic anhydride, are to be found, but these studies appear to have aroused in him only a passing interest. The work involved in the revision of Strecker's text-book, his academic and political duties, his translation to the Leipzig chair in 1885, were doubtless all in part responsible for the apparent falling off in importance of his contributions to chemical literature. The appearance in 1888 and 1889 of his epoch-making papers on space relations of the atoms in carbon compounds, on which he had pondered for many years, synchronised with a renewed activity in research work more commensurate with the expectations of the scientific world which knew his powers. From this time onwards his laboratory was the spring from which issued the stream of work which has helped to justify the use of those conceptions first foreshadowed by himself, and afterwards endowed with definite shape by the genius of van't Hoff.

Since the appearance of the original papers by Le Bel and van't Hoff, no serious attempt had been made to apply the theory to non-enantiomorphous isomerism, although van't Hoff had discussed the isomerism of compounds such as fumaric and maleïc acid in considerable detail. In order to explain the intraconversion of these two compounds, through the medium of the halogen derivatives of succinic acid, Wislicenus assumed that the groups on neighbouring carbon atoms act on one another in a manner determined by their "chemical affinities," and that in cases where these adjacent atoms are singly interbound, and hence doubtless free to rotate about the point of mutual attachment, such a rotation will take place as to lead to the adoption of the most favourable ("begünstigte") configuration. An arrangement so brought about would, he considered, be stable at low temperatures, but as the oscillations increased in violence with rise of temperature a new configuration might result.

In dealing with compounds of the type of fumaric and maleïc acids, and represented by the generalised formulæ

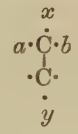
$$\begin{matrix} a\cdot C\cdot b \\ \| \\ b\cdot C\cdot a \end{matrix} \qquad \text{and} \qquad \begin{matrix} a\cdot C\cdot b \\ \| \\ a\cdot C\cdot b \end{matrix}$$

"Centrally" or "axially" symmetrical. "Plane" symmetrical.

he pointed out that, in the conversion of substances of the centrosymmetrical type into saturated compounds, it is a matter of indifference to which of the doubly-bound carbon atoms either part of the additive agent attaches itself, as the products are identical. In the planosymmetrical series, the products of addition are enantiomorphous, but in both cases there are equal chances that *either* of the two common "bonds" may be ruptured, as the molecule is symmetrical

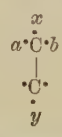
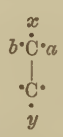
about the plane containing the groups affixed to the doubly-bound pair of carbon atoms. The last condition is also present in the more general case where any doubly-bound carbon atom is attached to two different groups,

except in the single instance where the molecule is already an asymmetric one, that is to say, where it already contains one or more asymmetric atoms, or is built on one of the types which comply with the conditions necessary for the existence of enantiomorphism, and to which attention was drawn by van't Hoff in his original treatise. It follows, therefore, that whilst, in general, by the conversion of a group

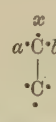
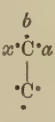
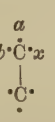
into a saturated one 

an asymmetric carbon atom is produced, the right- and left-handed individuals are formed in approximately equal numbers,[1] and thus the

[1] In accordance with the usual convention, the enantiomorphous forms here are

 and 

Throughout the following pages, however, only one of the two mirror images is represented in any instance, as the results here arrived at by the manipulation of the formulæ apply with equal truth to both, and such inactive mixtures will be indicated by the letter (*r*) affixed to the one formula given. It may be pointed out that a rotation of either carbon atom about the "bond" joining the two may be represented by an exchange in the position of the other three groups attached to that atom providing that their order, clockwise or counter-clockwise, around that carbon atom remains the same; thus, the three figures

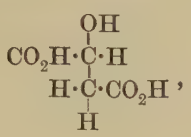
  and 

represent three phases in the rotation of the upper carbon atom about the vertical "bond," as the order *abx* about that atom is counter-clockwise in each case.

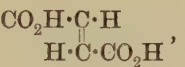
For numerous reasons, the parts of the agent added at a double binding will, in all cases, be represented as becoming attached in the mode above indicated, namely, in the line of the original ethylenic linkage, and, inversely, the withdrawal of two groups in the formation of an ethylenic union is imagined to occur only in the

non-production of optically active substances from inactive compounds of this class is at once accounted for.

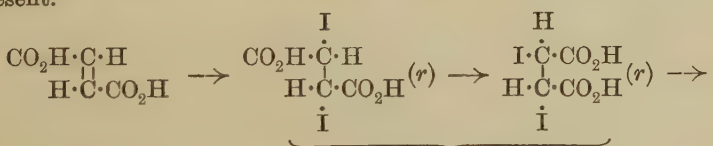
Malic acid, according to Wislicenus,[1] is probably to be regarded as constituted with opposed carboxyl groups



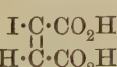
the affinity of the carboxyl group for hydrogen doubtless being greater than that of carboxyl for another carboxyl group or for hydroxyl, and the production of fumaric acid,



as the main product when the elements of water are withdrawn from malic acid is precisely in agreement with this assumption. The conversion of ethyl maleate into ethyl fumarate by means of iodine was explained by aid of the supposition that di-iodosuccinic acid is the initial product, and the mutual repulsion of the two iodine atoms then results in the rotation of the two parts of the molecule, a more favoured configuration being adopted; from the molecule in this new disposition hydrogen iodide is then withdrawn, a process leading to the production of iodomaleïc acid, which is afterwards converted into maleïc acid itself by the reducing action of the hydrogen iodide present.



Fumaric acid. Externally compensated di-iodosuccinic acid.



Iodomaleic acid.

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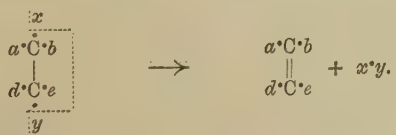
instance when they are represented on the paper as in a straight line with the "double bond" about to be formed:



[1] *Annalen*, 1888 **246**, 53—96.

The process by which hydrobromic acid effects the reverse change of maleïc into fumaric acid was shown to be capable of explanation on similar lines.

In the original memoir presented to the Königl. Sächs. Gesellschaft der Wissenschaften, attention was drawn to certain observations of Petrie and of Bandrowski which appeared to be inconsistent with the theory of the relations of maleïc and fumaric acids therein put forward. Petrie found that fumaric acid is the sole product of the action of bromine on maleïc acid in presence of water at ordinary temperatures, and Bandrowski obtained dibromosuccinic acid as the result of the interaction of bromine and acetylenedicarboxylic acid. Wislicenus was able to show later[1] that these reactions are in reality very complicated, the products being mixtures of a number of compounds such as his theory was capable of explaining.

In replying to certain criticisms of Lossen, Wislicenus took occasion to remark that the conception of atoms as mere material points was antagonistic to his views, for he regarded the atoms as aggregations of the primitive element and analogous to compound radicles, being, therefore, endowed with a space configuration of their own. To his mind it appeared not improbable that the carbon atom has a tetrahedral shape, and that the forces which are displayed in the "affinities" or "bonds" are concentrated in the four corners of this configuration, perhaps for reasons such as lead to the accumulation of the presumably analogous electric charge at the points and corners of a conductor; if so, the carriers of energy must be the primitive atoms, exactly as the chemical energy of compound radicles is the resultant of the energy of the elementary atoms.

Among the first compounds which Wislicenus proceeded to investigate, with the aid of his stereochemical ideas, were the isomeric tolane dichlorides.[2] By the immediate application of van 't Hoff's conception, it was concluded that the product obtained by the direct addition of chlorine to tolane must be the planosymmetric compound $\begin{matrix} C_6H_5\cdot C\cdot Cl \\ \| \\ C_6H_5\cdot C\cdot Cl \end{matrix}$, so that the isomeride of lower melting point is therefore to be represented by the axially symmetrical formula $\begin{matrix} C_6H_5\cdot C\cdot Cl \\ \| \\ Cl\cdot C\cdot C_6H_5 \end{matrix}$.

Wislicenus assigned to β-coumaric acid the structure $\begin{matrix} H\cdot C\cdot C_6H_5\cdot OH \\ \| \\ H\cdot C\cdot CO_2H \end{matrix}$, for the reason that it is more readily converted into the lactone, coumarin, than is the isomeric acid; in order to account for the conversion of the latter into coumarin by hydrogen bromide, the assumption was made that the elements of hydrogen bromide are

[1] *Annalen*, 1888, **246**, 53—96. [2] *Ibid.*, **248**, 1—34.

added at the ethylenic linkage, and that a subsequent internal rotation of the molecule takes place consequent on a supposed inclination towards the formation of the lactone.

The practical investigation of the isomeric crotonic acids fell to his pupils Teisler and Langbein.[1]

The results led him to infer that solid crotonic acid has the structure

$$\begin{matrix} H\cdot C\cdot CH_3 \\ \| \\ H\cdot C\cdot CO_2H \end{matrix}'$$

leaving for the liquid *iso*crotonic acid the formula

$$\begin{matrix} CH_3\cdot C\cdot H \\ \| \\ H\cdot C\cdot CO_2H \end{matrix}.$$

The former, with chlorine, yielded $\alpha\beta$-dichlorobutyric acid,

$$\begin{matrix} Cl \\ H\cdot \dot{C}\cdot CH_3 \\ H\cdot \dot{C}\cdot CO_2H \\ \dot{C}l \end{matrix} (r)$$

whilst $\alpha\beta$-*iso*dichlorobutyric acid, $\begin{matrix} Cl \\ CH_3\cdot \dot{C}\cdot H \\ H\cdot \dot{C}\cdot CO_2H \\ \dot{C}l \end{matrix} (r)$, was the product from *iso*crotonic acid. By removal of the elements of hydrogen chloride from $\alpha\beta$-*iso*dichlorobutyric acid, the product α-chlorocrotonic acid was obtained,

$$\underbrace{\begin{matrix} Cl \\ CH_3\cdot \dot{C}\cdot H \\ H\cdot \dot{C}\cdot CO_2H \\ \dot{C}l \end{matrix} (r) \longrightarrow \begin{matrix} Cl \\ CH_3\cdot \dot{C}\cdot H \\ CO_2H\cdot \dot{C}\cdot Cl \\ \dot{H} \end{matrix} (r)}_{\alpha\beta\text{-}iso\text{Dichlorobutyric acid.}} \longrightarrow \underbrace{\begin{matrix} CH_3\cdot C\cdot H \\ \| \\ CO_2H\cdot C\cdot Cl \end{matrix}'}_{\alpha\text{-Chlorocrotonic acid.}}$$

and the same substance, when warmed with an aqueous solution of sodium carbonate, by simultaneous loss of carbon dioxide and hydrogen bromide afforded α-*iso*chloropropylene, $\begin{matrix} CH_3\cdot C\cdot H \\ \| \\ H\cdot C\cdot Cl \end{matrix}$; the latter was rapidly attacked by alkalis at 100°, yielding allylene, $\begin{matrix} CH_3\cdot C \\ \| \\ H\cdot C \end{matrix}$, whilst the isomeric α-chloropropylene, $\begin{matrix} CH_3\cdot C\cdot H \\ \| \\ Cl\cdot C\cdot H \end{matrix}'$, prepared by a similar series of reactions, applied to crotonic acid, reacted with alkalis very much more

[1] *Annalen*, 1888, **248**, 281—355.

slowly, a result which is in harmony with the structures assigned to the isomeric crotonic acids.

The additional observation was made that by heating *aβ*-dichlorobutyric acid a partial conversion of the compound in *aβ-iso*dichlorobutyric acid may be effected.

The study of the relations subsisting between angelic and tiglic acids gave results of an equally interesting character.[1]

Tiglic acid, represented by the formula $\begin{matrix}H\cdot C\cdot CH_3\\ \|\\ CH_3\cdot C\cdot CO_2H\end{matrix}$, gives a dibromide which, when warmed with sodium carbonate in aqueous solution, is converted into crotonylene hydrobromide,

$$\begin{matrix}H\cdot C\cdot CH_3\\ \|\\ CH_3\cdot C\cdot CO_2H\end{matrix} \longrightarrow \underbrace{\begin{matrix}Br\\ H\cdot\dot{C}\cdot CH_3\\ |\\ CH_3\cdot C\cdot CO_2H\\ |\\ \dot{B}r\end{matrix}\ (r) \longrightarrow \begin{matrix}Br\\ H\cdot\dot{C}\cdot CH_3\\ |\\ Br\cdot C\cdot CH_3\\ |\\ \dot{C}O_2H\end{matrix}\ (r)}_{\text{Tiglic acid dibromide.}} \longrightarrow \begin{matrix}H\cdot C\cdot CH_3\\ \|\\ Br\cdot C\cdot CH_3\end{matrix};$$

Tiglic acid. Crotonylene hydrobromide.

the isomeric angelic acid yielded in his hands as main product angelic acid dibromide, a compound which had previously been overlooked, and which with sodium carbonate was found to yield *iso*dibromo*pseudo*butylene,

$$\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot CO_2H\end{matrix} \longrightarrow \underbrace{\begin{matrix}Br\\ CH_3\cdot\dot{C}\cdot H\\ |\\ CH_3\cdot C\cdot CO_2H\\ |\\ \dot{B}r\end{matrix}\ (r) \longrightarrow \begin{matrix}Br\\ CH_3\cdot\dot{C}\cdot H\\ |\\ Br\cdot C\cdot CH_3\\ |\\ \dot{C}O_2H\end{matrix}\ (r)}_{\text{Angelic acid dibromide.}} \longrightarrow \begin{matrix}CH_3\cdot C\cdot H\\ \|\\ Br\cdot C\cdot CH_3\end{matrix}.$$

Angelic acid. *iso*Bromo*pseudo*butylene.

The last-named substance was also obtained by removal of the elements of hydrogen bromide from *pseudo*butylene dibromide,

$$\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot H\end{matrix} \longrightarrow \underbrace{\begin{matrix}Br\\ CH_3\cdot\dot{C}\cdot H\\ |\\ CH_3\cdot C\cdot H\\ |\\ \dot{B}r\end{matrix}\ (r) \longrightarrow \begin{matrix}Br\\ CH_3\cdot\dot{C}\cdot H\\ |\\ Br\cdot C\cdot CH_3\\ |\\ \dot{H}\end{matrix}\ (r)}_{\text{pseudo Butylenedibromide.}} \longrightarrow \begin{matrix}CH_3\cdot C\cdot H\\ \|\\ Br\cdot C\cdot CH_3\end{matrix}.$$

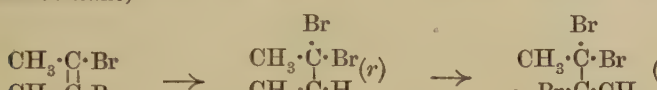
*pseudo*Butylene. *iso*Bromo*pseudo*butylene.

[1] *Annalen*, 1893, **272**, 1—99; 1893, **274**, 99—119; 1900, **313**, 207—209, 210—228.

Crotonylene, with bromine, gave $\beta\gamma$-dibromo*pseudo*butylene,

Crotonylene. $\beta\gamma$-Dibromo*pseudo*butylene.

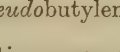
the isomeride of which, namely, $\beta\gamma$-*iso*dibromo*pseudo*butylene, was prepared by removing the elements of hydrogen bromide from $\beta\gamma\gamma$-tribromobutane,

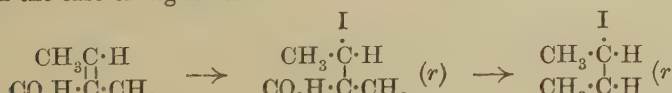


$\beta\gamma$-Dibromo*pseudo*butylene. $\beta\gamma\gamma$-Tribromobutane.

iso-$\beta\gamma$-Dibromo*pseudo*butylene.

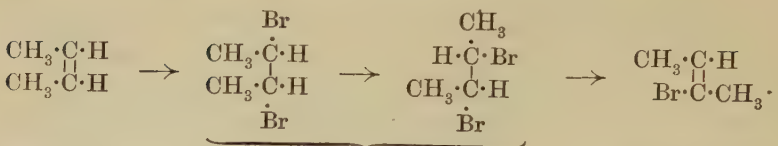
From both of these dibromo*pseudo*butylenes, the same crotonylene tetrabromide was obtained by addition of bromine.

The hope expressed by Wislicenus in this paper that it might some day be found possible to prepare the hydrobromides of angelic and tiglic acids, and afterwards to convert these into the isomeric *pseudo*-butylenes, was, strictly speaking, not realised, although some time later the same end was attained by the employment of the hydriodides of these two acids.[1] Tiglic acid hydriodide, warmed with an aqueous solution of sodium carbonate, lost hydrogen iodide and carbon dioxide, affording a hydrocarbon which, when passed into bromine, gave rise to a dibromide; the latter, on treatment with potassium hydroxide, was converted into *iso*bromo*pseudo*butylene,  . Angelic acid, by the same series of reactions, was finally transformed into bromo-*pseudo*butylene proper, . These results are exactly in accordance with the general conclusions which Wislicenus had previously drawn, and the changes may be followed in a graphic manner in the case of tiglic acid:—



Tiglic acid. Tiglic acid hydriodide.

[1] Wislicenus, Talbot, and Henze, *Annalen*, 1900, **313**, 228—242.



*pseudo*Butylene. *pseudo*Butylene dibromide (meso). *iso*Bromo*pseudo*-butylene.

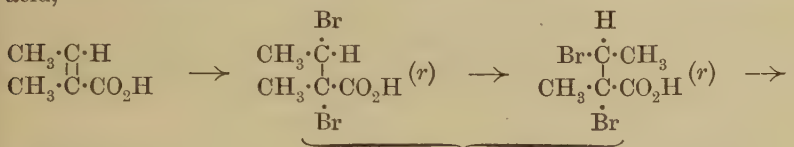
Fittig and Pagenstecher had actually observed that angelic acid when brominated yielded tiglic acid dibromide as main product; the difference between these results and those of Wislicenus and Pückert proved to be due to the fact that unless a low temperature be maintained during the addition of bromine, and strong light carefully excluded, isomeric change of the angelic to tiglic dibromide may occur. Wislicenus was not disposed to assume an undue amount of credit for his discovery of the true dibromide of angelic acid which Fittig and Pagenstecher had overlooked, but drew attention to the circumstance that the draught cupboards in Fittig's laboratory at Strassburg were placed in the windows, and thus received a strong light, whilst in his own laboratory at Leipzig they lay between the windows, otherwise, as he remarked, angelic acid dibromide might have remained unknown.[1]

Later, with Schmidt, Wislicenus prepared *pseudo*butylene by the method employed by Le Bel and Greene, namely, by the dehydration of *iso*butyl alcohol. It was found[2] that a mixture of the centrosymmetrical and planosymmetrical hydrocarbons was formed, and the mixture of dibromides made by passing the mixture of hydrocarbons into bromine was separated into two portions by fractional distillation. The higher boiling portion, on treatment with potassium hydroxide, yielded the bromo-derivative of the planosymmetrical *pseudo*butylene, $\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot Br\end{matrix}$, in larger quantity than did the lower boiling fraction, but the main product from both was the bromo-derivative of the centrosymmetrical hydrocarbon, $\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ Br\cdot C\cdot CH_3\end{matrix}$, which in presence of hydrogen bromide or on exposure to sunlight was found to undergo a slow conversion into its stereoisomeride. Of the two bromo*pseudo*-butylenes, the one assigned the formula $\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot Br\end{matrix}$ gave crotonylene the more readily when heated with potassium hydroxide, an observation quite in accordance with the relative position of the hydrogen and bromine atoms in the formulæ assigned.

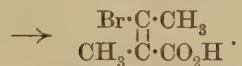
Henze assisted in adducing new evidence in support of Wislicenus's

[1] *Annalen*, 1893, **272**, 98. [2] *Ibid.*, 1900, **313**, 210—228.

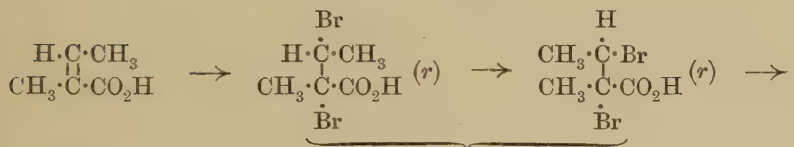
view.[1] The dibromide of angelic acid, as was anticipated, yielded β-bromotiglic acid under the influence of strong potassium hydroxide, whilst the dibromide of tiglic acid was converted into β-bromoangelic acid,



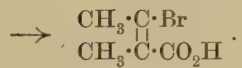
Angelic acid. Angelic acid dibromide.



β-Bromotiglic acid.

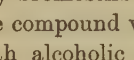


Tiglic acid. Tiglic acid dibromide.

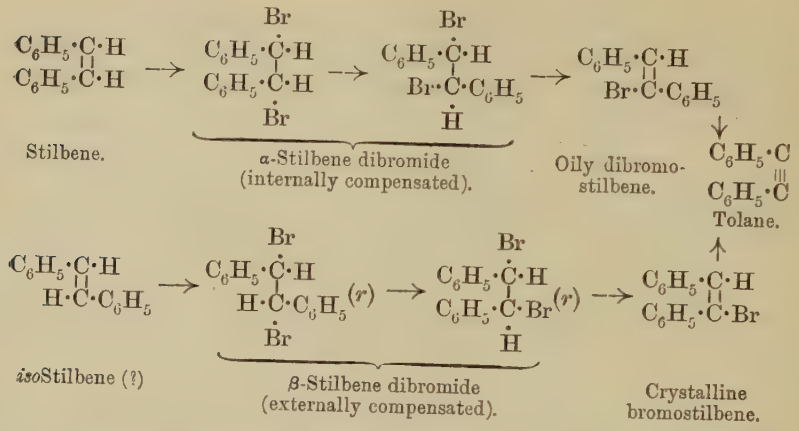


β-Bromoangelic acid.

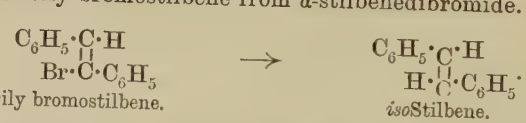
Of these β-bromo-unsaturated acids, the latter was the more easily converted into crotonylene by means of sodium carbonate solution, an observation which again is in harmony with the conclusions previously formed, as this isomeride is the one to which was assigned the formula having the bromine atom and the carboxyl group in the position most favourable to the occurrence of this change.

Stilbene gave Wislicenus and Seeler two dibromides, the main product being the α-derivative, which was considered to be the normal product, although, unlike the great majority of such normal addition products, it was found to be produced in larger proportion at a high temperature and in presence of intense light.[2] Either dibromide, when heated, underwent a partial conversion into the other; both yielded monobromostilbenes on treatment with alkalis, the α-compound affording an oily bromostilbene, the latter a crystalline one, and of these the crystalline compound was the more easily converted into tolane when boiled with alcoholic potassium hydroxide, showing that it has the structure  . These observations led to the following view of the changes studied :—

[1] *Annalen*, 1900, **313**, 243—250. [2] *Ber.*, 1895, **28**, 2693—2703.

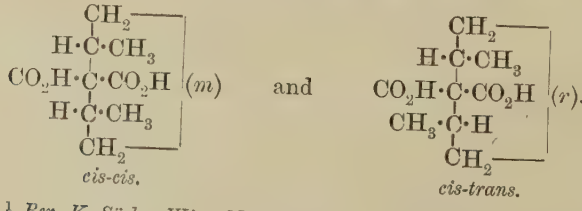


Although at the time no direct evidence as to the existence of isomeric stilbenes could be adduced, Wislicenus with Jahrmarkt afterwards succeeded in obtaining centrosymmetrical *iso*stilbene [1] by reducing the oily bromostilbene from α-stilbenedibromide.



This hydrocarbon, unlike stilbene itself, is a liquid which yields ordinary stilbene when distilled under atmospheric pressure, or when left with traces of bromine or iodine; when dissolved in carbon disulphide and mixed with bromine in absence of light it gives β-stilbene dibromide to the extent of 83 per cent. of that theoretically possible.

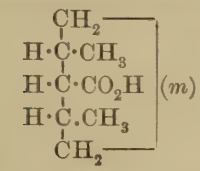
The investigation of stereoisomerism in cyclic compounds led Wislicenus, with Peters, Schramm and Mohr, to a study of the isomeric forms of ββ′-dibromohexane.[2] On heating this dibromo-compound with ethyl disodiomalonate, an oil having the composition of a diethyl dimethyl*cyclo*pentanedicarboxylate was formed, and this, on hydrolysis, afforded a mixture of ester-acids, dicarboxylic acids, and monocarboxylic acids, each of which was shown to be related to one or other of the two dimethyl*cyclo*pentanedicarboxylic acids,



[1] *Ber. K. Sächs. Wiss. Math. Phys. Ch.*, 1900, **52**, 117—123.
[2] *Ber.*, 1901, **34**, 2565—2583.

The constitution of the two acids was ascertained by heating them so as to cause the loss of one molecular proportion of carbon dioxide, and in these circumstances one of them gave rise to two stereoisomeric monocarboxylic acids, and the other to one monocarboxylic acid only. The former must have been produced from the *cis-cis* derivative and the latter from the *cis-trans*-one.

The formulæ of the isomerides from the *cis-cis*-dicarboxylic acid are



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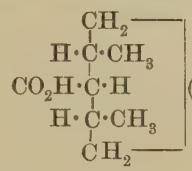
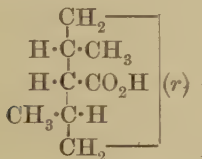
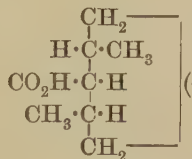


and represent internally compensated inactive compounds. Those of the possible products arising from the *cis-trans*-dicarboxylic acid, in the same manner, are

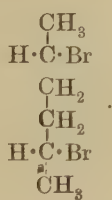


and



but these are in reality identical, and represent one of the two enantiomorphous forms of an inactive mixture.

The $\beta\beta'$-dibromohexane employed was separated by freezing into two parts, one solid and the other a liquid; the former of these, when condensed with ethyl disodiomalonate, afforded ethyl *cis cis*-dimethyl*cyclo*pentanedicarboxylate, and was, therefore, the meso-compound



the liquid isomeride, on the other hand, gave rise to the *cis-trans*-dicarboxylic derivative, and was, therefore, an inactive mixture of the *d*- and *l*-compounds.

It is perhaps hardly necessary to say that the foregoing sketch deals only with a part of the scientific work which was carried out by Wislicenus himself or by his pupils under his direction. No mention has been made of his recent contributions to the study of

the reactions of dichloroether,[1] his investigations on the interaction of chloral with ketones,[2] on adipinketone,[3] of his discovery of the true vinylacetic acid,[4] or of his numerous researches on the stereoisomerism of the cyclic pinacones obtained by the reduction of diketones.[5] To each of these much interest attaches, but considerations of space have led me to select from his more recent work that part which appears to have the most importance in connection with the growth of the science of stereochemistry, with which his name is indissolubly connected.

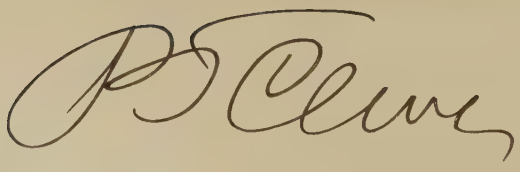
During the last few years of his life, Wislicenus became more and more the victim of severe attacks of ill-health, against which he fought with all his fine energy and determination, working steadily almost to the last. In the summer of 1902, he found his most strenuous efforts at resistance unavailing, and at last took refuge in complete rest at health resorts. His condition in the autumn gave his friends cause for the gravest anxiety, and early in the morning of December 5th, 1902, he passed away.

Two days later, a mournful but impressive ceremony was seen in the lecture-room attached to the Leipzig Chemical Laboratory; Beckmann, Ostwald, His, Lüty, Hantzsch, Medicus, and Bucher, colleagues of Wislicenus, representing their respective departments and faculties, expressed in moving terms their appreciation of the exalted and many-sided character of their departed friend.

The concluding words which fell from Ostwald were these:—"Und wenn wir betrachtend vor ihnen stehen, so fühlen wir es lebendig; du warst nicht nur ein grosser Forscher, du warst auch ein guter Mensch!" and this is the note which persistently rings in the memory of all who have tried to understand the man.

There can be no doubt that in Wislicenus the world lost a man, not only of great and many-sided ability, but also of extraordinary directness of purpose and splendid character.

[1] *Annalen*, 1884, **226**, 261—281; 1888, **243**, 151—192.
[2] *Ber.*, 1893, **26**, 908—915.
[3] *Annalen*, 1893, **275**, 312—382.
[4] *Ber.*, 1899, **32**, 2047—2048.
[5] *Annalen*, 1898, **302**, 191—244.



CLEVE MEMORIAL LECTURE.

Delivered on June 21st, 1906.

By Thomas Edward Thorpe, C.B., F.R.S.

No circumstance in the national and personal history of experimental science is more remarkable than the position which Sweden and the Swedes occupy in relation to chemistry. When regard is had to her position among Continental nations—to her chequered political history, to her geographical isolation, the comparative sparseness of her population, her relative poverty, the fewness of her seats of learning—the influence which Sweden has been able to exert on the development of that branch of science which it is the proper function of this Society to foster must always excite our wonder, admiration, and gratitude. The mere mention of the names of Bergmann, Scheele, Berzelius, Mosander, Gadolin, Nilson, is sufficient to remind us how great have been her services to the science of chemistry.

In Per Theodor Cleve, who was elected a Foreign Member of this Society in 1883, we had a man who throughout a strenuous life, wholly devoted to academic pursuits, and to the cultivation of pure science, worthily upheld and handed forward the traditions which his countrymen had succeeded in associating with his calling and particular office. In compliance with our custom, and at the request of the Council, I am privileged this evening to offer you some account of the life work of our deceased Foreign Member.

I owe the invitation doubtless to the circumstance that I enjoyed the personal acquaintance and friendship of Cleve, who for some years past did me the honour to accept of my hospitality during his visits to London. Although I had thereby opportunity of learning at first hand something of his personal history and of his achievements, and of noting his mental and intellectual characteristics and of forming impressions such as can only be acquired by social intercourse and personal contact, I am conscious that my account of the man and of his work owes whatever of completeness it may possess to the assistance which has been afforded to me in its compilation by Cleve's daughter and her husband. On learning of the duty which had been imposed upon me by your Council, Dr. and Mrs. Euler were good enough to forward to me an advance copy of the obituary notice which they were preparing for the *Berichte* of the German Chemical Society, and which has now been published. Of this account I have, with their permission, made full use in putting together what I have to tell you this evening.

Per Theodor Cleve was born in Stockholm on February 10th, 1840. He was the thirteenth child of the merchant F. T. Cleve, whose ancestors had emigrated from Western Germany and settled in Sweden during the middle of the eighteenth century. It is told of the young Cleve that even during his school-time his leaning towards natural science, and especially towards natural history, was strongly marked, and that he spent hours which should have been devoted to classical studies in rambling round the country in search of animals, plants and stones—to the despair of the philologs, who set him down, as they had previously done his great countryman Berzelius, as a youth of very little promise. This love for natural history was an abiding passion with Cleve, and constantly struggled with, and in the end conquered, his allegiance to chemistry. Destiny, indeed, intended that he should be a naturalist: the stress of circumstance only made him a chemist. The boyish love of rambling strengthened into a constant yearning for foreign travel. His sympathy with the natural objects around his home—with the birds and flowers of his native woods and fields, and the many wonderful minerals in his native rocks—grew into an intense desire to see and to know Nature in her every mood, and under many skies. Had fortune favoured him Cleve would probably have followed in the footsteps of Humboldt and Darwin, and spent his life in scientific travel; compelling circumstances kept him for the most part at home, and in the end made him what he was.

Although it is clear that Cleve's predilections were towards an academic life, it is not very obvious why he became a chemist. It may have been that the outlook as regards natural history was not very hopeful: Scandinavia forty years ago was not as convinced as now of the supreme importance to her national prosperity of those studies to which Cleve was inclined. As regards chemistry the times were more propitious. The early 'sixties was a period of great unrest in that science, and, as we all know, it culminated in nothing less than a revolution. Although speculation and theory had never much attraction for Cleve, the young *candidat* could not have been wholly uninfluenced by the movement of the time, or insensible to the effect it was exerting on the development of chemistry. Be this as it may, Cleve, who after five years' residence at Upsala had taken his degree, became when twenty-three years of age a lecturer on Organic Chemistry in the University. At that time the Chair on General Chemistry at Upsala was held by Lars Svanberg, who almost exclusively occupied himself with mineralogical inquiries. He was a fairly prolific contributor to the literature on mineral chemistry of the period, and occasionally associated himself with his students in mineral analyses, but Cleve apparently

owed little to his teaching and still less to his example or encouragement.

Cleve's earliest contribution to chemical literature, made when he was twenty-one years of age, was "On Some Ammoniacal Chromium Compounds," and consisted in an extension of the work of Frémy, by whom this interesting class of substances was first made known. The chromammonium derivatives are among the most complicated and perplexing of inorganic compounds, and their discovery undoubtedly gave a great extension to the conception of isomerism in mineral chemistry. Cleve thus early entered on a field of inquiry which occupied him for several years, and which has taxed the energies of many successive investigators, notably Jörgensen and Christensen. Cleve's first communication definitely established the existence and fixed the composition of the initial member of the chromtetrammonium series, namely chlorochromtetrammonium chloride, $Cl_2 \cdot Cr_2 \cdot 8NH_3Cl_4 \cdot 2H_2O$, or, as he termed it, *tetramminchromchlorid*, a salt forming beautiful deep red trimetric crystals.

The study of isomerism, using that term in its widest sense, and the influence of structure and constitution on the properties of bodies, may be said to have been the guiding principle which actuated the major part of Cleve's experimental labours, whether in inorganic or organic chemistry. The most cursory inspection of his published work shows that this was the dominant, underlying motive of his inquiries—the silver thread which ran, as it were, through the fabric he elaborated. This fact requires to be borne in mind, in justice to Cleve, as indicating his philosophic habit of mind, and the real objective of his intellectual activity. Accident and opportunity no doubt at times appeared to change the main current of his thoughts; his mind was too active not to perceive and even occasionally to follow the many side-issues to which his inquiries gave rise, but with a true economy he invariably returned to what he recognised to be the proper direction of his energies. Singleness of aim and tenacity of purpose are the hall-marks of every successful prosecutor of scientific inquiry, and Cleve possessed these characteristics in an eminent degree.

His work on the chromammonium compounds naturally led him to undertake the investigation of similar groups of inorganic substances, in the hope of further elucidation of the problems in which he was interested, and he next occupied himself with the study of the platinum bases, the chemistry of which was even in a more chaotic condition than that of the more recently discovered chromium compounds. The history of the platinum bases, or platinammines, takes its rise from the discovery by Magnus

in 1828 of the famous "green salt" with which his name is associated, and which he prepared by the action of aqueous ammonia on platinous chloride. Ten years later, Gros, under Liebig's direction, obtained a series of chlorinated derivatives of this salt, containing the group NO_3, and shortly afterwards Reiset prepared the base $Pt(NH_3)_4(OH)_2$, of which the compounds prepared by Gros and the green salt of Magnus were regarded as salts.

The relation between these substances was expressed as follows:—

Reiset's first base	$Pt(NH_3)_4(OH)_2$.
Gros's salt	$Cl_2Pt(NH_3)_4(NO_3)_2$.
Green salt of Magnus.....	$Pt(NH_3)_4 \cdot PtCl_4$.

In 1844 Reiset obtained a second series of salts containing only half as much ammonia as the first series, and from which a new base could be prepared—the so-called Reiset's second base. Peyrone some time afterwards prepared a chloride which had the same composition as the chloride of Reiset's second base, namely, $PtCl_2 \cdot 2NH_3$, but which was altogether different from it in properties. Isomerism among inorganic substances was at that time unknown, and to Berzelius, who first gave us the term, was inconceivable. Personal friendship and trust in Wöhler may have predisposed him in the first instance to tolerate the existence of isomerism among carbon compounds, to which his own work on tartaric acid may have further inclined him, as something exceptional and peculiar to organic substances, but, in the main, to Berzelius identity of composition meant identity of character: there was no room in his system for inorganic isomerides, and Peyrone's discovery was met by flat incredulity. But evidence as to its truth steadily accumulated. Raewsky discovered the analogues to Gros's compounds, and Gerhardt and Laurent made known the existence of the platinammine salts. The theoretical aspect of these facts was everywhere recognised as of the highest importance. They constituted so many test cases by which the sufficiency of a doctrine which had long dominated chemistry could be tried, and served to augment the slowly accumulating body of testimony which eventually overthrew it. Driven to recognise the existence of these compounds, Berzelius made futile efforts to reconcile them with his electro-chemical system. But the inadequacy of these attempts was apparent to all but the blindest adherents of the Swedish school. On the other hand, Gerhardt, by an extension of the theory of types, gave a more or less plausible explanation of the mode of structure and constitution of these groups of substances, which was not out of harmony with prevalent conceptions, and which, indeed,

in some respects, foreshadowed present-day developments in its recognition of variable valency. But the swing of the pendulum is not confined to that particular department of intellectual activity we call politics; we have constant examples of it in every sphere of human thought, for the movement is eventually controlled and regulated by the gravitational tendency which is inherent in the truth itself. The explanations of Berzelius might be partial and imperfect, but the underlying truth in his doctrine could never be wholly obscured, and when the system of types, as a theory of chemistry, in its turn gave way to a more rational generalisation, what there was of permanent value in both became incorporated in the new philosophy.

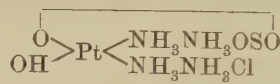
As I have said, the theoretical significance of these compounds was very generally recognised, and in this connection I may recall the early work of Buckton, extending from 1851 to 1854, and of Hadow, published in our Journal for 1866.

It was at about this period that Cleve undertook the study of the ammonia platinum compounds. He had, of course, been reared under the doctrine of Berzelius, whose influence, indeed, was paramount in Sweden long after it had waned in the rest of Europe, and he had no disposition or inducement at the time to trouble himself about its limitations. Speculative chemistry had never, at any period, much attraction for Cleve. In this respect he resembled Bunsen, with whose mental characteristics he had other points of resemblance and sympathy. His first papers on the platinum bases, published by the Royal Society of Sciences of Upsala, are, therefore, as might have been anticipated, written wholly in the spirit and from the standpoint of an adherent of the orthodox school of chemical philosophy in Sweden. He was induced, he says, to undertake the investigation of these substances as a sequel to his work on the chromammonium compounds in the hope of eventually obtaining an independent view of the general constitution of the metal-ammonia compounds. The first object of his inquiry was sufficiently modest; it was to determine the position of the chlorine in the salts obtained from Gros's base. Gros's base he found to be free from halogen; it could be regarded as an oxidised derivative of Reiset's first base. The salts obtained by Gros, as well as those of Raewsky, were, in fact, derivable from the hydroxyl compound

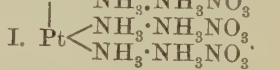
$$(OH)_2Pt(NH_3)_4(OH)_2.$$

a formula which further serves to indicate one of the most remarkable properties of its salts, namely, that the halogens and acid radicles which they may contain are not removable with equal facility. Thus, for example, the four chlorine atoms in Gros's

chloride are not equally precipitable by silver nitrate, a fact which may be explained by saying that it contains two chlorine ions and two undissociated chlorine atoms. One of the sulphates prepared by Cleve had the same empirical composition as a basic sulphate derived from Gros's base, but only one of the three equivalents of sulphuric acid was precipitable by barium salts. From this salt he prepared a platinum base, which he termed *Sulphatodiplatinammin*, and to which he subsequently gave the formula



Some of the early work on the platinum bases, more particularly that on Gros's compounds, was done in Würtz's laboratory in Paris, but in 1868 Cleve returned to Sweden and worked for some months in the mineralogical laboratory of the Stockholm Academy of Sciences. Here he discovered an entirely new series of these complicated compounds, which he obtained by the action of ammonia on the iodine derivatives of Gros's base. They were the first representatives of these bases containing the double platinum atoms, and were termed by him the diplatinammin compounds. He eventually gave to them the following rational formula:—



In his attempt to gain a true conception of the constitution of the metal-ammonia bases Cleve undoubtedly obtained great assistance from Blomstrand, and there is no question that the "Chemie der Jetztzeit," which was published in Heidelberg in 1869, and in which Blomstrand developed and extended his views of the mutual relations of these various groups of substances into an orderly and systematic arrangement, gave Cleve his first clear insight into their constitution and intradependence. The effect on him was immediate, and is to be seen in his next memoir in 1870 on the isomeric platinum bases, in which he finally renounces the Berzelian system of representation and notation in favour of the more comprehensive and rational scheme, founded on valency, which still satisfies us.

In this paper he describes a number of derivatives of Reiset's second base, as well as a series of salts isomeric with these. The first members of these latter salts were discovered by Peyrone, but their true relations remained hitherto obscure. These compounds were termed by Cleve the platinoxydulammonium salts. His

study of the properties of the two isomeric series led him to suggest the following formulæ as expressing their constitution:—

$$Pt\begin{matrix}<\\ \end{matrix}\begin{matrix}NH_3Cl\\ NH_3Cl\end{matrix} \qquad\qquad Pt\begin{matrix}<\\ \end{matrix}\begin{matrix}NH_3\cdot NH_3Cl\\ Cl\end{matrix}.$$

Chloride of Reiset's second base. Platinoxydulammonium chloride.

Cleve further found that tetravalent platinum gave rise to a series of salts, obtained from platinoxydammonium, isomeric with Gerhardt's platinammine compounds. The two series of compounds discovered by Cleve, $Pt(NH_3\cdot NH_3R)R$ and

$$R_2Pt(NH_3\cdot NH_3R)R,$$

were subsequently termed by Blomstrand, whose classification and nomenclature of the platinammonium compounds is still commonly adopted, the platososemidiammines and platinsemidiammines, whereas the isomeric bases of Reiset, $Pt(NH_3R)_2$, and Gerhardt, $R_2Pt(NH_3R)_2$, were styled respectively platosammines and platinammines.

In order to obtain further experimental support for his views of the constitution of these isomerides, Cleve studied their behaviour towards aniline. He found that in the case of the compound obtained from the platosammine chloride the two aniline molecules were readily split off, whereas in that derived from the platosemidiammine chloride a molecule of aniline remained. In the first case we had

$$Pt\begin{matrix}<\\ \end{matrix}\begin{matrix}NH_3Cl\\ NH_3Cl'\end{matrix}$$

whilst in the second we had, according to Cleve,

$$Pt\begin{matrix}<\\ \end{matrix}\begin{matrix}NH_3Cl\\ C_6H_5NH_2Cl\end{matrix}.$$

Cleve's view that both classes of salts contain divalent platinum is, however, hardly probable in view of Jörgensen's later work. The constitution of the corresponding chlorides would seem, on the whole, to be better represented by the formulæ

$$Pt\begin{matrix}<\\ \end{matrix}\begin{matrix}NH_3Cl\\ NH_3Cl\end{matrix} \quad \text{and} \quad Cl\cdot Pt\begin{matrix}<\\ \end{matrix}\begin{matrix}NH_3\\ NH_3Cl'\end{matrix},$$

although Cleve's expression has the merit of clearly indicating the important fact of the different behaviour of the chlorine in the two isomeric chlorides.

This paper was followed (1871) by a short communication in which Cleve explained the relation between the green salt of Magnus, platodiammine chloride platinous chloride,

$$Pt(NH_3\cdot NH_3Cl)_2\cdot PtCl_2,$$

and the brown salt discovered by Peyrone—the first member of the platosamminesemidiammine series—

$$2Pt\begin{matrix}<^{NH_3\cdot NH_3Cl}_{NH_3Cl}\end{matrix} + PtCl_2.$$

The chloride $Pt\begin{matrix}<^{NH_3NH_3Cl}_{NH_3Cl}\end{matrix}$ may be caused to combine with two atoms of chlorine, when it forms $Pt\begin{matrix}<^{Cl}_{NH_3NH_3Cl}\\<^{NH_3Cl}_{Cl}\end{matrix}$.

The corresponding platinamminesemidiammine derivatives were also prepared by Cleve.

In the same year he published two papers on the sulphites and nitrites of the isomeric bases of platosammine and platosemidiammine.

The work on the ammoniacal platinum bases occupied Cleve nearly six years, and he put together his results in a remarkable memoir, written in English and published by the Swedish Academy of Sciences in 1872, a copy of which is to be found in our Library. In this memoir, which extends to upwards of 100 4to. pages, Cleve arranges all the known derivatives of the ammoniacal platinum bases in accordance with Blomstrand's scheme of classification, using his system of terminology. The whole of these bodies—many hundreds in number—may be grouped under three main divisions, each division being subdivided into several series, as follows:—

Group I.—*Plato- or Platoso-compounds.*

Series I. Platosemiammines, $RPtNH_3R$.
,, II. Platosammines, $Pt(NH_3R)_2$.
,, III. Platodiammines, $Pt(NH_3NH_3R)_2$.
,, IV. Platosemidiammines, $Pt(NH_3\cdot NH_3\cdot R)R$.
,, V. Platomonodiammines, $Pt(NH_3\cdot NH_3R)(NH_2R)$.

Group II.—*Platini- or Platin-compounds.*

Series I. Platinammines, $R_2Pt(NH_3R)_2$.
,, II. Platinidiammines, $R_2Pt(NH_3\cdot NH_3R)_2$.
,, III. Platinisemidiammines, $R_2Pt(NH_3\cdot NH_3R)R$.
,, IV. Platinimonodiammines, $R_2Pt(NH_3\cdot NH_3)R(NH_3R)$.
,, V. Platinitriammines, $R_2Pt(NH_3\cdot NH_3\cdot NH_3R)_2$.

Group III.—*Diplatinum Compounds.*

Series I. Diplatodiammines, $\left|\begin{matrix}Pt(NH_3\cdot NH_3R)\\ Pt(NH_3\cdot NH_3R)\end{matrix}\right.$.

Series II. Diplatosodiammines, $\left|\begin{matrix}RPt(NH_3\cdot NH_3R)\\ RPt(NH_3\cdot NH_3R)\end{matrix}\right.$,

or $\left|\begin{matrix}Pt(NH_3\cdot NH_3R)\\ R_2Pt(NH_3\cdot NH_3R)\end{matrix}\right.$.

Series III. Diplatinammines $\left|\begin{matrix}RPt(NH_3R)_2\\ RPt(NH_3R)_2\end{matrix}\right.$.

Series IV. Diplatinidiammines $\left|\begin{matrix}RPt(NH_3\cdot NH_3R)_2\\ RPt(NH_3\cdot NH_3R)_2\end{matrix}\right.$.

Although Cleve entitles his memoir "On Ammoniacal Platinum Bases," its subject-matter really comprehends the discussion and systematic arrangement of all the metalline ammoniacal bases and their salts at that time known, and must have involved great labour and research in its compilation.

From this review of all the known ammoniacal compounds of the different metals Cleve concluded:—

I. The highest number of molecules of ammonia which occur united together in ammoniacal compounds is 4. *Tetrammines* of calcium, strontium, and perhaps of cuprosum are as yet the only ones known.

II. *Triammines* are formed by calcium, magnesium, cobalt, nickel, zinc, cadmium, silver, rhodium and iridium.

III. *Diammines* are produced by most metals.

IV. Consequently, as a rule, the most positive metals seem to have the power of uniting the greatest number of molecules of ammonia, but more negative metals, such as platinum, form the most stable ammoniacal compounds.*

During some portion of the time over which this work extended, Cleve found opportunity to gratify his inclination towards the study of natural history. Shortly after his return from Paris he

* The prefixes *mono-*, *di-*, &c., denote the number of NH_3 groups directly united with one another, and not the number of such groups in direct union with the Pt atom. Thus, as the compounds in Series III, Group II, contain $(NH_3\cdot NH_3)$ or one diammine chain, they are called *semi-diammines*; and as those in Series IV, Group II, contain one diammine and one monoammine chain, they are termed *mono-diammines*.

was enabled, by means of a grant from the Stockholm Academy of Sciences, to undertake a journey to the West Indies with a view to an inquiry into the geological structure of the Antilles, the results of which were published in 1871 in English, by the Swedish Academy.

On his return he was made Adjunct in Chemistry in what was then known as the Stockholm Technological Institute, but which has now developed into a polytechnic of the type of Charlottenburg or Zurich. Whilst occupying this position he did a considerable amount of literary work, compiling text-books and putting together many contributions to the periodical literature of the time on botanical and geological subjects. On Svanberg's retirement he was called to the Chair of Chemistry in Upsala, where he remained until the age-limit of sixty-five which operates in Sweden required him to resign the Professorship.

Shortly before his removal from the Swedish capital to Upsala, Cleve turned his attention to the study of the rare earths—a branch of chemical inquiry with which the names of Scandinavian investigators are pre-eminently associated. As is well known, Sweden has the good fortune to possess an uncommon share of those minerals which are characterised by containing the so-called rare earths—one small locality alone, namely, Ytterby, not far from Stockholm, was famous as the happy hunting-ground of the collector—and the investigation of this material was long the monopoly of Swedish chemists, as the names of Gadolin, Ekeberg, Mosander, Berzelius, Hisinger, and Bahr testify. The greater part of their work in this special department of mineral chemistry was done during the first third of the nineteenth century, and resulted in the addition of no fewer than seven substances to the list of the chemical elements then known, namely, yttrium, cerium, thorium, lanthanum, didymium, terbium, and erbium. The death of Berzelius and the consequent disappearance of his school, together with the extraordinary development of organic chemistry, due mainly to Liebig and his associates in Germany, and to Dumas, Laurent and Gerhardt, and others in France, undoubtedly checked the progress of inquiry in the special field which the Swedish chemists had cultivated with such brilliant success. But the discovery of the remarkable absorption spectrum of didymium by Gladstone, and of that of erbium by Bahr, led to renewed activity in rare-earth chemistry, and the services of the spectroscope as an analytical instrument were at once brought into requisition in connection with this department of inorganic chemistry.

It was at this juncture that Cleve and his collaborator Höglund entered the field, and in a paper published in 1872 they gave the

results of an inquiry which covered much the same ground as a prior investigation by Bahr and Bunsen on the gadolinite earths.

Incidentally, however, Cleve and Höglund prepared a large number of hitherto undescribed salts of yttrium and erbium, both of which they regarded at that time as divalent elements.

The publication by Mendeléeff of the epoch-making memoir in which he first made known the great generalisation which is associated with his name resulted in further attention being paid to the chemistry of the rare earths. As will be remembered, Mendeléeff in this paper discussed the position of certain of the rare-earth metals in the periodic system, and showed that all the known facts rendered it in the highest degree probable that the greater number of these elements must be regarded as belonging to the third group of his scheme of classification. Cleve at once recognised that the systematic study of this group of elements in the light of Mendeléeff's generalisation would constitute one of the strongest tests of its validity. He repeated and extended his work with Höglund on the compounds of yttrium and erbium, and then attacked the chemistry of the elements thorium, lanthanum, and didymium. No stronger evidence of Cleve's power of work could be adduced than is shown in the monograph published in 1874, embodying the results of the two years' labour, on the compounds of these five metals. Concurrently with this inquiry, Jolin, under Cleve's direction, took up the study of the salts of cerium. As the result of this comprehensive investigation, Cleve established that thorium is certainly a quadrivalent element, whilst the other metals constitute a natural group of chemically related bodies, of which cerium and lanthanum, on the one hand, and yttrium and erbium on the other, form subgroups, the respective members of which stand in close relationship to each other, their compounds, as Marignac and Topsoë had shown, being respectively isomorphous; whereas didymium would appear to occupy an intermediate position, as it forms salts which are isomorphous sometimes with the one subgroup and sometimes with the other. If we assume with Cleve that lanthanum is to be regarded as trivalent, it follows that the remaining four elements are also trivalent, a conclusion which Cleve sought to establish by the preparation of a large number of typical salts. Cleve's main conclusions were not universally accepted at the time of their publication, and indeed were freely criticised by Delafontaine and by Wyrouboff, but all subsequent inquiry has served to establish their validity, and the position of these elements in the schemes of classification at present in vogue is practically that which Cleve indicated.

Some years later, and mainly in consequence of the work of

Frerichs and Smith, Cleve was induced to repeat certain of his observations on the compounds of lanthanum and didymium. He confirmed his results, with, however, this significant difference, that for the first time he was led to give expression to his doubt as to the individuality of didymium. He founded this surmise mainly on the behaviour of didymium oxide on heating, the change in colour suggesting the presence of another element.

How well founded was this surmise was established by Auer von Welsbach in 1885 by the discovery of praseodymium.

In the years immediately following the publication of Cleve's papers, the chemistry of the rare-earth metals received important extensions by the discovery of ytterbium by Marignac and of scandium by Nilson. Shortly after the existence of the latter element was made known, Cleve was enabled to prepare a number of its salts, and to make the first determinations of its atomic weight, with the result of proving that scandium was identical with Mendeléeff's ekaboron. It is hardly necessary to remind you of the effect on the chemical world of this discovery. It was the second instance of the realisation of Mendeléeff's prediction as to the existence of hitherto unknown elements the properties of which he had been able to forecast by the aid of the principles he first clearly indicated. The realisation of these predictions, coming so soon after the promulgation of the Periodic Law, did more to secure its general acceptance among men of science than any other set of facts.

Marignac's discovery of ytterbium in what was generally regarded as a homogeneous earth rendered it almost certain that the properties up to that time associated with erbia were not those of an individual substance, and accordingly Cleve set himself to prepare pure erbia with a view to an accurate study of its characters and a redetermination of its atomic weight. No erbia that Cleve could at the outset obtain furnished constant atomic weight values, and he concluded, therefore, that Mosander's erbia was even a more complicated mixture than had hitherto been surmised. Thalén's investigation of the spectroscopic behaviour of the several fractions obtained by Cleve showed that they contained, in addition, possibly, to other substances, at least two new elements, one having an atomic weight between that of erbium and of yttrium—that is between 166 and 89, and the other having an atomic weight between those of erbium and ytterbium—that is between 166 and 173. The former Cleve named *holmium*, the latter he called *thulium*. Holmium appears from its spectroscopic indications to be identical with Soret's X. It is still doubtful, however, whether holmia and thulia are actually simple substances; there is good reason to believe, indeed, that Cleve's holmia is in reality a mixture containing possibly unknown elements.

Unfortunately, these substances are present in the gadolinite earths in extremely small quantity, and their separation is both tedious and imperfect.

Although Cleve was unable to do more than indicate the probable existence of these new elements in gadolinite, he eventually succeeded in obtaining pure erbia, and the atomic weight which we now associate with that element is based upon his determinations.

The discoveries made subsequent to 1874 led Cleve to undertake a revision of his determinations of the atomic weights of yttrium, lanthanum and didymium. As regards yttrium and lanthanum, the repetition resulted in comparatively unimportant changes; in the case of didymium the number was much too high, owing to the presence of samarium, prior to that time unknown. The number obtained by Cleve on repetition was 142, almost the arithmetic mean of the atomic weights of its two subsequently discovered components, praseodymium, 140·5, and neodymium, 143·6.

Cleve next studied the action of hydrogen dioxide upon the rare earths, and described a number of their peroxides, and in 1883 and 1885 he published important papers on samarium and its salts, and gave the first accurate estimation of its atomic weight.

These constituted his last contributions to this department of mineral chemistry, although he continued to the end to take an interest in its further development, placing the stores of material which he had accumulated in the Upsala laboratory at the disposal of such of his students as were willing to devote themselves to its investigation, and who were, at the same time, capable of taking advantage of the advice and counsel which his own ripe experience enabled him to give. It is only necessary to name the monographs on praseodymium by Schéele, on ytterbium by Astrid Cleve, on gadolinium by Benedicks, and on neodymium by Holmberg, to show that these treasures have been turned to good account.

As is well known to all here, the rare earths have acquired an increased importance within recent times owing to their technical value in connection with artificial illumination, and the whole world is now being searched for new sources of supply. Even now undreamt-of amounts of certain of them resulting from the operations needed to extract the commercially valuable oxides are at the disposal of investigators, and we may confidently anticipate, therefore, fresh additions to knowledge in a field of inquiry where much still remains to be done.

Cleve's services to inorganic chemistry, and especially to rare-earth chemistry, were recognised by the Royal Society in 1894 by the award to him of the Davy Medal. In presenting the medal, the President, Lord Kelvin, said: "This field of inquiry is pre-eminently Scandinavian. By the manner in which he has cultivated

it, Professor Cleve has shown himself a worthy successor of such forerunners as Gadolin, Berzelius and Mosander, and by sound and patient investigation he has faithfully upheld the traditions inseparably associated with these names. All chemists are agreed that no department of their science demands greater insight or more analytical skill than this particular section. Many of the minerals which furnish the starting point for investigation are extremely rare, and the amounts of the several earths which they contain are frequently very small. Moreover, the substances themselves are most difficult of isolation, and their characters are so nearly allied that the greatest care and judgment are required in order to determine their individuality. A remarkable example of Professor Cleve's power in overcoming these difficulties is seen in his masterly inquiry into the affinities and relations of the element scandium, discovered by Nilson. This, one of the rarest of the metals, is found only in gadolinite to the extent of 0·003 per cent.; and in yttrotitanite to the extent of about 0·005 per cent. The whole amount of the material, as oxide, at Cleve's disposal was only about 1 gram, but with this small quantity he determined the atomic weight of the element, and ascertained the characters of its salts with such precision as to leave no doubt of the identity of scandium with the element *Ekabor*, the existence of which was predicted by Mendeléeff, in the memorable paper in which he first enunciated the Law of Periodicity. Cleve's research, indeed, constitutes one of the most brilliant proofs of the soundness of the great generalisation which science owes to the Russian chemist.

"A not less remarkable instance of Cleve's skill as a worker is seen in his research on samarium and its compounds, which he communicated, as one of its Honorary Foreign Fellows, to the Chemical Society of London. The existence of samarium was inferred independently by Delafontaine and Lecoq de Boisbaudran, but we owe to Cleve the first comprehensive investigation of its characters and chemical relations. From the nature of its compounds, a large number of which were first prepared and quantitatively analysed by Cleve, and from the value of its atomic weight, which was first definitely established by him, it would appear that samarium most probably fills a gap in the eighth group of Mendeléeff's system."

And perhaps I may be pardoned for saying that there is no circumstance in my official connection with the Royal Society which I have greater pleasure in recalling than the share I was permitted to take, as a member of its Council, in thus testifying to the appreciation which all British chemists feel of the value of Cleve's services to their science.

Cleve's name is associated with descriptive mineralogy in con-

nection with a mineral first made known by Nordenskjöld in 1878, and which is of importance from its relation to the history of argon and helium. It will be remembered that Hillebrand, in 1890, announced that gaseous nitrogen was a constituent of cleveite. Shortly after the discovery of argon, Cleve directed his pupil Langlet to make a further investigation of the gases in this mineral. The results of this inquiry were, however, anticipated by Ramsay, who discovered that the characteristic gases of cleveite were helium and argon. Langlet made use of the helium thus extracted to make the first accurate determinations of its atomic weight, and obtained the value He = 4·0 which finds its place in our tables.

As director of the Upsala laboratory, then, as now, the most important school of chemistry in Sweden, Cleve was anxious to secure for organic chemistry its proper position in the scheme of instruction in the University. Since the death of Berzelius, Sweden had mainly won her laurels in the fields of mineral chemistry, but no teacher in Cleve's position could be unmindful of the extraordinary development of the chemistry of the carbon compounds which had resulted from the activity of French and German workers, or oblivious of the material benefits which followed from the technical applications of their discoveries.

It was incumbent on him, therefore, to arrange that Upsala should take her due share in the cultivation of this great and rapidly extending branch of inquiry. Although it might be expected that Cleve's predilections as a worker would be to continue in the line of investigation with which he had been associated for so many years past, and in connection with which he had accumulated such rich stores of material, he determined to embark himself upon the great ocean of organic research with such of his pupils as were disposed to accompany him. As might have been surmised, he was mainly attracted by problems of isomerism and constitution, and he found in the chemistry of naphthalene ample scope for the exercise of his powers. Cleve began by attacking the constitution of the nitrosulphonic acids. This he and Atterberg sought to unravel by converting them into the corresponding dichloronaphthalenes by the methods of Carius, Koninck and Marquardt. This field of inquiry occupied the Upsala laboratory for about eighteen years. When Cleve entered it only two of the ten possible dichloronaphthalenes were known. He himself prepared six of the isomerides, and Atterberg obtained two more in addition. Only those who have occupied themselves with work of this character can fully realise how tedious and time-consuming it is owing to the very slight differences in physical characters which certain of the substances possess.

The nitrosulphonic acids prepared by Cleve of which he was able to determine the constitution were the 1·5, the 1·6, 1·3, 1·7, 1·8 and 1·4. He also prepared the corresponding amino-acids, of which the 1·6 and 1·7 are of special importance in the colour industry, and are known in technology as Cleve's naphthylaminesulpho-acids.

Cleve and his pupil Arnell also prepared and studied eight of the fourteen possible chloronaphthalenesulphonic acids, namely, the 1·4, 2·6, 2·8, 1·5, 1·6, 1·3, 1·2 and 1·7 isomerides, and he further prepared many of the nitro-compounds, the constitution of which he determined by conversion into the trichloronaphthalenes. Other coadjutors in this work in the Upsala laboratory were Jolin, Widman, Ekstrand, Forsling and Ekbom.

In awarding the Davy Medal Lord Kelvin also made allusion to the naphthalene work, and to the manner in which Cleve had thus gradually brought order out of confusion, adding that: "Within recent years a score of workers have occupied themselves with the same field of research, and no greater proof of Cleve's accuracy and care as an investigator could be furnished than the manner in which his naphthalene work—confessedly one of the most intricate and complicated sections of the chemistry of aromatic compounds—has stood the ordeal of revision."

No account of the outcome of the Upsala laboratory whilst under Cleve's direction would be complete without some allusion to the fact that it was during that period and in that place that Svante Arrhenius acquired his knowledge of chemical science. The celebrated memoir of 1884 in which Arrhenius first promulgated the theory which has made him famous was his Doctor-Dissertation at Upsala.

Cleve, who, I have good grounds for stating, greatly appreciated his honorary membership of our Society, published several of his contributions to the literature of chemistry in our Journals. Among these was his first memoir on samarium, which appeared in our Transactions in 1883. He also published a short note in our Proceedings, in 1891, on the formation of an explosive substance from ether. Lastly I may remind you of the obligation which the Society is under to him for the admirable critical estimate of the life-work of his friend Marignac which forms the memorial lecture on our distinguished Foreign Member.

Although Cleve continued to the end of his academic career to interest himself in the proper work of his chair, reading the periodical literature of our science with regularity, and studying to keep himself informed of its development, towards the close of his life he became more and more absorbed in those biological studies to which he had never ceased to be attracted, and latterly

he gave himself entirely to them. Of his work on the diatoms and on plankton—most of which was published in English—this is not the place to speak, even if I were competent to offer any opinion concerning it. That it should have secured for him the honorary membership of the Royal Microscopical Society—a distinction which he prized not less than his fellowship in our Society—is some evidence of the value which contemporary workers set upon his labours.

When the time for his retirement from the Chair at Upsala arrived, he moved to Gothenburg that he might be near the sea and in touch with the hydrographic station at Bornö, and thus pursue uninterruptedly and in quietude the study of his beloved plankton. Of a sound constitution and of good bodily strength, regular and methodical in his habits, active in mind, serene in temper, and unimpaired in intellectual vigour, he might still at sixty-five look forward to many years of scientific activity. But these years were not to be his. In December of 1904 he was suddenly seized with pleurisy. His heart became affected, and cardiac asthma supervened. In the spring of 1905 he was somewhat better and journeyed to Upsala, but died there, within three weeks of his arrival, on the 18th of June, 1905.

His memory will be cherished by those who had the privilege of his friendship as that of a true man, vigorous in intellect, rich in mental acquirement, wide in sympathy with every branch of natural science, courteous in manner, calm and unimpassioned in judgment, of a humour ironical at times and even mordant, but withal tolerant and large-hearted, and of a flexibility of opinion, especially on theoretical questions, which was often disconcerting to his friends. And in the annals of science his name will continue to live as that of one who followed her unselfishly and gave unstintedly to her service all that was best in him.

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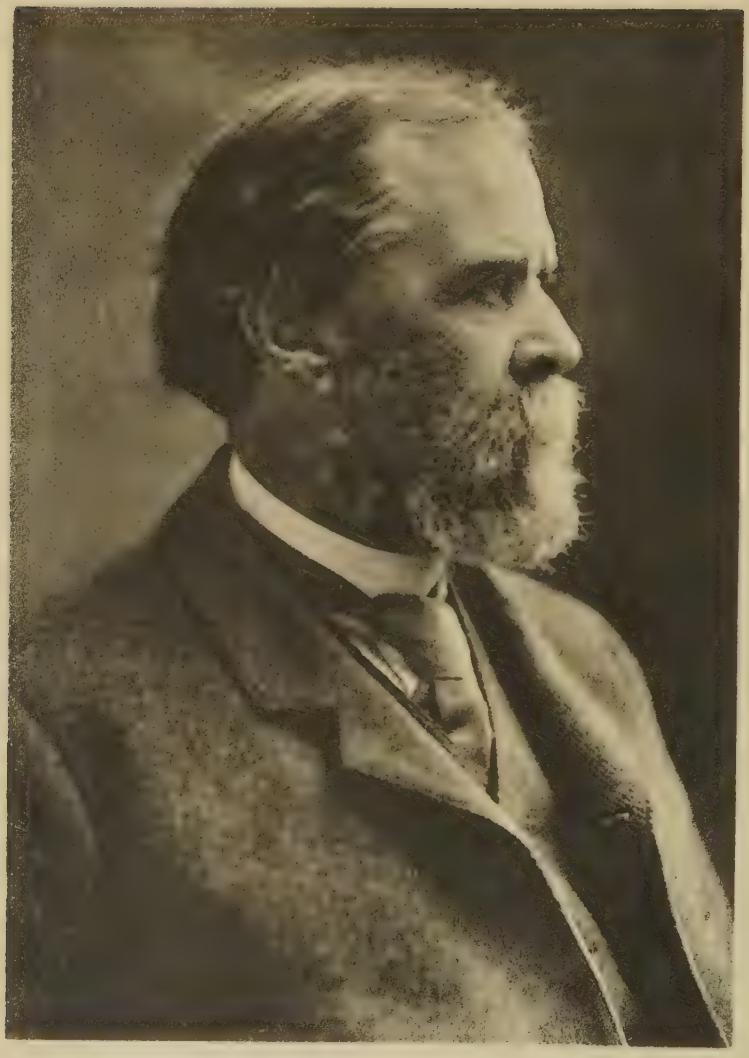

WOLCOTT GIBBS MEMORIAL LECTURE.

Delivered on June 3rd, 1909.

By Frank Wigglesworth Clarke.

It is easy to write biography when one is satisfied with a mere chronicle of events. But to clothe the skeleton of fact with flesh and blood, so that the man shall, as it were, live again, is difficult, and yet, figuratively speaking, that seems to be the sort of task which you have set before me. What manner of man was Wolcott Gibbs? What influences helped to mould his character? What did he do, and under what conditions was his work accomplished? These are the questions which I must try to answer.

Oliver Wolcott Gibbs (he dropped the Oliver early in his career) was born in the city of New York, on February 21, 1822. His father, Colonel George Gibbs, was a man of some wealth, who owned a large country place at Sunswick, on Long Island, not far from the then small city. He was an enthusiastic mineralogist, and gathered a collection which, ultimately sold to Yale College, became the nucleus of the great cabinet since made famous by the labours of the two Danas, Brush, and Penfield. It was perhaps the control of the Gibbs collection which first led J. D. Dana to write his classical *System of Mineralogy*. Colonel Gibbs, after whom the mineral *gibbsite* was named, was himself the author of several memoirs upon mineralogical subjects, and his eldest son, also named George, achieved some reputation as a geologist and as a student of ethnology. Wolcott Gibbs was born into an atmosphere of scientific interests, and his early associations must have influenced his choice of a career. A taste for science ran in the family.

Laura Gibbs, the mother of Wolcott, came of distinguished ancestry. Her father, Oliver Wolcott, rose through various positions to that of Secretary of the United States Treasury, a post which he held during the latter part of Washington's administration and well into the administration following. He then became a Justice of the United States Circuit Court, and during the last ten years of his life he was Governor of the State of Connecticut. His father, another Oliver, was a magistrate, a major-general of militia, a member of Congress, and a signer of the American Declaration of Independence. He, too, was a Governor of Connecticut, and so also was his father, Roger Wolcott, the first noteworthy member of the line. In short, the ancestors of Wolcott Gibbs were people of far more than average

ability, who had the confidence and esteem of their fellow citizens, and were therefore entrusted with positions of high rank and responsibility. Even though there was no commanding genius among them, no man of world-wide fame, they at least left to their descendants a legacy of lofty examples, well worthy of emulation. We may differ in our opinions as to the significance of heredity; but we can recognise the fact that Gibbs received from his forbears a sound mind in a sound body, together with traditions of well-doing that could not be disregarded. A good ancestry is a good beginning for any man.

In his early environment Gibbs was also fortunate. Although he was only eleven years old when he lost his father, his mother survived for many years, and gave him the best of opportunities for healthy development. She was a woman of strong character and unusual ability, and her home became a centre in which the best intellectual society of New York was to be found. Her character, forceful, positive, patriotic, and public-spirited, was reflected in that of her son.

The early childhood of Wolcott Gibbs was largely spent at his father's estate of Sunswick, where, as he tells us in a brief autobiographical note, "he was often occupied with making volcanoes with such materials as he could obtain, and in searching the stone walls . . . for minerals, and the gardens and fields for flowers." At the age of seven he was sent to a private school in Boston, where he was under the care of a maiden aunt, whose sister had married the famous Unitarian divine, William Ellery Channing. The winters were passed in Boston, and the summers with the Channings at their country place near Newport, Rhode Island. Here again he was surrounded by choice influences, and saw many distinguished people. The reputation of Dr. Channing attracted many visitors, including more than a few from abroad, and the boy must have come to some extent in contact with them. Being but a child, he may not have understood or appreciated his opportunities, but his imagination could not have been entirely unaffected. His early associations foreshadowed his later career.

When he was twelve years old, Gibbs returned to New York, and began his preparation for college. In 1837 he entered Columbia College as a freshman, and graduated in 1841. It was in his junior year that he published his first scientific paper, a description of a new form of galvanic battery, in which carbon was used, probably for the first time, as the inactive plate. This achievement, unimportant as it may seem now, was really remarkable in two ways; first, on account of the youth of the author, and, secondly, because of the conditions under which the work was

done. In those days the American colleges, like the public schools of England, were intensely classical in their aims, and science received the minimum of attention. Latin, Greek, and mathematics ruled the curriculum, with only a smattering of other subjects. Even in the classics literature was subordinate to grammar, and as for the modern languages they were almost, if not quite, ignored. What science was cultivated was taught by lectures and text-book recitations, for the era of laboratory instruction had not begun. That a pupil of eighteen should make an original investigation under such conditions was surprising, but it showed the irresistible tendencies at work in his mind. The early impulses, received from his father, could not be overcome.

After receiving his bachelor's degree, young Gibbs went to Philadelphia, where he served as assistant in the laboratory of Robert Hare, the well-known inventor of the compound blow-pipe, who was then Professor of Chemistry in the Medical School of the University of Pennsylvania. Gibbs's purpose was to fit himself for holding a similar professorship, and so, after several months of experience with Hare, he entered the College of Physicians and Surgeons in New York, and in 1845 became a full-fledged Doctor of Medicine. He never practised, and probably never intended to do so, for the study of chemistry was the main purpose of his life, and his medical studies were only a means to an end. Indeed, they stood him in good stead when, many years later, he undertook to study the physiological effects of isomeric organic substances on animals.

Up to this point the training of the future chemist had been only preliminary, a laying of foundations, so to speak. In his time advanced scientific education was not easily obtained in America, and ambitious students who were able to do so sought their higher opportunities in Germany. Accordingly, Doctor Gibbs, as we must now call him, went abroad, and began by spending several months with Rammelsberg in Berlin. After this he studied for a year under Heinrich Rose, which was followed by a semester with Liebig at Giessen. He next went to Paris, where he attended lectures by Laurent, Dumas, and Regnault, and in 1848 he returned home, ready to begin the real labours of his life. Among his teachers the one who most impressed him was Rose, whom Gibbs greatly admired, and who doubtless gave his pupil his strong bias towards analytical and inorganic chemistry. From his other teachers, however, Gibbs acquired a breadth of view and an insight into different fields of research, which made him all the stronger as an investigator. He was a chemist in the largest sense of the term, and not a mere sub-specialist.

After returning to America, Gibbs first delivered a short course of lectures at a small college in Delaware. Then, in 1849, his native city claimed his services, and he was appointed professor of chemistry in the newly established Free Academy, now the College of the City of New York. He remained in this position for fourteen years, chiefly occupied in teaching elementary students, and at first doing, apparently, little else. He was not idle by any means, but he was finding himself, and his time was not wasted. In was in 1857 that his first really notable research was given to the world, namely, the joint memoir of Gibbs and Genth on the ammonio-cobalt bases. Of this I shall speak more at length later. In 1851 he became an associate editor of the American Journal of Science, and began the preparation of a series of abstracts which brought the results of foreign investigations to the attention of American readers. These abstracts amounted in all to about 500 pages, and, despite their brevity, were conspicuously clear and comprehensive. In 1861 the first of his papers on the platinum metals appeared, and his reputation was at last firmly established.

Notwithstanding his recognised ability, Dr. Gibbs, during this period, suffered one serious disappointment. The chair of chemistry in his *alma mater*, Columbia College, became vacant, and Gibbs, backed by the recommendations of nearly all the leading men of science in America, was a candidate for the position. He was, however, a Unitarian, and Columbia was then an institution under sectarian control. Purely on religious grounds, his candidacy was rejected, and a man of far smaller attainments received the appointment. This was unfortunate for Columbia, but not altogether so for Gibbs. In 1863 he was called to a more desirable post, the Rumford Professorship in Harvard University. Nominally, this was a professorship of the "Application of Science to the Useful Arts," but its incumbent, in addition to lecturing on heat and light, was expected to take charge of the chemical laboratory in the Lawrence Scientific School, and this gave Gibbs a great opportunity for usefulness. Furthermore, the position was a delightful one on its social side, and he was thrown into close association with many congenial spirits. There were Louis Agassiz the zoologist, Asa Gray the botanist, Jeffries Wyman in comparative anatomy, Benjamin Pierce in mathematics, and J. P. Cooke in chemistry. Literature was represented by Longfellow, Lowell, Holmes, and other less famous writers; altogether an aggregation of distinguished men which could not be matched elsewhere in America, or equalled at few places in the world. Gibbs was among his peers, and in a place where his worth could be fully appreciated.

Dr. Gibbs remained in charge of the Scientific School laboratory for eight years, and during that time his researches were, for the great part, although not exclusively, devoted to analytical methods. The school was technically a department of Harvard University, and yet its work was carried on quite independently. The students were usually men of definite purposes, who knew what they wanted and went where it could be best obtained. They went to Agassiz for zoology, to Gray for botany, and to Gibbs for chemistry, because those men were the leaders in their respective subjects, and they worked, not in classes, but as individuals. The students in chemistry had little or nothing to do with the students in other branches, for the school was distinctly professional in its aims. Teachers from other institutions, seeking to enlarge their knowledge, were often among them. Gibbs was now training men who intended to become chemists, and some among them were qualified to assist in his investigations. Moreover, he was not overloaded by numbers, for he rarely had more than twenty students in attendance at any one time. There was one assistant, to relieve him of routine work; his lectures on light and heat cost him little effort, and he was therefore able to devote his energies to research more advantageously than ever before.

It was my good fortune to have been a student under Gibbs during the greater part of four years, from 1865 until 1869. I may therefore be permitted to speak of his teaching from my own experience, believing that in such matters the personal note is not without value. There was nothing unusual about the course of instruction so far as ordinary details went, for that necessarily followed certain well-established lines. Most of the students had already gained some elementary knowledge of chemistry; their work began with the usual practice in analytical methods and chemical manipulations, and as the men showed capacity they were admitted to the confidence of their master and aided him in his investigations. This procedure may seem commonplace enough to-day, but in the years of which I speak it was new to American institutions, and was looked upon doubtfully by some of the old-fashioned pedagogues. The students who chose to do so attended the excellent chemical lectures of Cooke in Harvard College, but that work was wholly optional. The only formal examination was the final examination for the bachelor's degree, and therefore there was no cramming for examinations. Gibbs apparently believed, although his belief was not stated in set terms, that a good teacher who kept in touch with his pupils should know perfectly well where they stood, and no examination could tell him anything more. In fact, examinations are often misleading, for the reason that even a fine scholar of nervous temperament may become confused

and helpless during the ordeal, and fail to answer the simplest questions. On the other hand, a poor student with a fair memory may cram for an examination, pass triumphantly, and amount to nothing afterwards. The real examinations under Gibbs were daily interviews, when he visited each student at his laboratory table and questioned him about his work. This, together with the reported analyses, gave the teacher a clear conception of the true standing of each man. The fewness of the pupils was a distinct advantage, for all worked together in one room, beginners and research students often side by side. The result was that they learned much from one another, and there were many discussions among them over the burning problems of the day. The men were taught to stand on their own feet, and to think for themselves, laying thereby a foundation for professional success which was pretty substantial. The course of instruction had no definite term of years prescribed for it, and graduation came whenever the individual had done the required amount of work and submitted an acceptable original thesis. The final examination was usually oral, each man alone with his master, and was conducted in an easy conversational way which tended to establish the confidence of the candidate from the very beginning. In my own case I remember that the questions covered a fairly broad range of chemical topics, and at the end of it Dr. Gibbs drew me into a sort of discussion or argument with him over the then modern doctrine of valency. I now see that his purpose was not merely to ascertain what I had read on the subject, but what I really thought about it, if indeed I was entitled to think at all. Gibbs invariably treated his students, not as so many vessels into which knowledge was to be poured, but as reasonable beings, with definite purposes, to whom his help must be given. That help was never denied to any man who showed himself at all worthy of it. The research work in which the advanced students shared, and for which they received public credit, served to teach them that chemistry was a living and growing subject, and to train them in the art of solving unsolved problems. They were taught to *do*, and encouraged to *think*, and if, on going forth into the world, they sometimes felt themselves qualified to revolutionise all science, their vanity did no harm and was soon remedied. An enlightened ignorance is only gained with advancing years, and the enthusiastic beginner cannot be expected to appreciate it. It is the last polish that the ripened scholar acquires.

What now is the meaning of this long disquisition upon the methods of Gibbs's laboratory? What was there at all unusual in his teaching? Nothing, perhaps, from a modern point of view,

but much that was new to America in the middle 'sixties. It was Gibbs's peculiar merit that he, more than any other one man, introduced into the United States the German conception of research as a means of chemical instruction, a conception which is now taken as a matter of course without thought of its origin. Gibbs worked with small resources and no help from outside; he was a reformer who never preached reform; his students rarely suspected that they were doing anything out of the ordinary; but they had the utmost confidence in their master, and took it for granted that his methods were sound. There was nothing of the drill master about Gibbs, no trace of pedantry, no ostentation of profound learning; but the students never doubted his sincerity of purpose and interest in their work, nor questioned his ability as a teacher. As for Gibbs himself, it is doubtful whether he ever imagined that his teaching was at all remarkable. He did what was to him the natural and obvious thing to do, simply and without pretence, and the results justified his policy. The success of his students is perhaps the best monument to his memory.

In 1871 the chemical instruction at Harvard University was reorganised, in spite of vigorous protests from Gibbs and many other leaders in science. The laboratory of the Scientific School was consolidated with that of the College, and Gibbs had no more students in chemistry. His work was limited to that of the Rumford professorship, a change which left him more time for personal research, but took from the students the inspiration of his teaching. The change may have been justifiable on grounds of economy, but it was otherwise a mistake, and it was so recognised among chemists generally. The economy was only financial; but an important asset of the University, the ability of a great teacher, was not turned to the best account. Fortunately for Gibbs, he had independent means, although he was not a rich man, and he was able to equip a small laboratory of his own and to employ a private assistant. In that laboratory he carried out those brilliant researches on the complex inorganic acids which marked the culmination of his career. The equipment was most modest, and in some respects it reminded one of the famous kitchen of Berzelius. Indeed, Gibbs's favourite piece of apparatus was that homely utensil, a cast-iron cooking stove, which served for several useful purposes. Precipitates could be dried in the oven, crucibles were buried in the coals, water was kept hot on top of it. As an instrument of research it was neither elegant nor orthodox, but it did the work, and what more could be desired? Gibbs adapted himself to circumstances, and cared little for the instrumental refinements which so many chemists seem to regard as necessary.

The real essentials were provided; mere conveniences, the luxuries of research, he could do without.

For sixteen years after the closing of the Scientific School laboratory, Dr. Gibbs lectured to small classes of students on the spectroscope and on thermodynamics. In 1887 he retired, as Professor-Emeritus, and went to live in his house at Newport, where he had been accustomed to spend his summer vacations. His private laboratory was moved to Newport also, and there he continued his investigations until, enfeebled by old age, he was obliged to rest on his laurels. As a recreation, he cultivated a flower garden, and was proudest of his roses. In that way his love of the beautiful found its chief expression. On December 9, 1908, he passed away, at the age of nearly eighty-seven. His wife, whose maiden name was Josephine Mauran, and whom he had married in 1853, died several years earlier, leaving no children.

So much for biography. It now remains for us to consider the contributions of Gibbs to science, and to trace their relations, so far as may be practicable, to later work. An investigation never stands alone; each one touches other investigations at several points; and its worth may be greatest as the progenitor of later researches. The suggestiveness of a discovery, its influence in stimulating thought, is fully as important as its immediate outcome. It is a seed, whose value is finally determined by its fertility.

Gibbs's first paper, a "Description of a New Form of Magneto-Electric Machine, and an Account of a Carbon Battery of Considerable Energy," published when he was a junior student at Columbia, has already been mentioned. In 1844 he attempted to discuss the theory of compound salt radicles, and in 1847, while a student abroad, he published a number of mineral analyses. In 1850, Gibbs pointed out the interesting fact that compounds which change colour when heated do so in the direction of the red end of the spectrum. In 1852 he published the first of his memoirs upon analytical methods, in which he proposed the separation of manganese from zinc by means of lead peroxide; and in 1853 he prepared, and partly described, an arsenical derivative of valeric acid. In all of this work there was nothing of great importance, but its varied character is suggestive. It represents the efforts of an active mind, feeling its way under unfavourable conditions, and not quite sure of its true capacities. Mineral chemistry, organic chemistry, analytical chemistry, chemical theory, and physics, in turn attracted his attention during this formative period of his career. It was in the great research on the ammonio-cobalt bases that Gibbs finally found himself, and forced the world to recognise his ability. His apprenticeship was ended, and his work as a master had begun.

The first of the ammonio-cobalt compounds, the oxalate of luteocobalt, was prepared by Gmelin in 1822, the very year in which Gibbs was born. It was supposed, however, to be a salt of cobaltic acid, and several other chemists, who studied it later, shared in the same misapprehension. In 1847, Genth, then at Marburg, discovered other salts of these bases, but it was not until 1851, after his emigration to America, that he published his description of them in a rather obscure journal. Genth was the first to recognise the true character of the new compounds, and he was followed by Claudet and Fremy, the three chemists working independently of one another and almost simultaneously. Up to this point Fremy's work was the most exhaustive, but it left much to be desired.

Genth had identified the two bases since known as luteocobalt and roseocobalt. In 1852 Gibbs discovered the salts of xantho-cobalt, which contained, in addition to the ammonia, a nitro-group. It was therefore quite natural that the two chemists should join forces, and in 1856 their celebrated memoir appeared. In this memoir thirty-five salts of the four bases roseocobalt, purpureo-cobalt, luteocobalt, and xanthocobalt were described, with adequate analyses, and, in eleven cases, crystallographic measurements by J. D. Dana. The roseo- and purpureo-compounds were for the first time clearly discriminated, although they were supposed to be isomeric, a misconception which could hardly have been avoided at that time. There was also an elaborate theoretical discussion on the constitution of the bases, but that also was premature. The fundamental theories of structure were yet to be developed. Blomstrand, Jörgensen, and Werner, in later years, utilised the data of Gibbs and Genth, and Werner especially made the ammonio-cobalt compounds the base of his famous theory of the constitution of the metal-amines. Gibbs and Genth laid the foundations, on which later investigators have built an imposing structure.

Gibbs was an experimentalist rather than a theorist, and yet he neither underrated nor avoided theory. In 1867 he published a paper on atomicities, or valences as they are now called, in which he developed the idea, then vaguely held by others, of residual affinities. He argued in favour of the quadrivalency of oxygen, and showed that on that supposition a molecule of water must be bivalent, and any chain of water molecules would be bivalent also. He then considered ammonia in the same way, with the two bonds of quinquevalent nitrogen unsatisfied. Ammonia, therefore, was weakly bivalent, and so, too, would be a chain of ammonia molecules. This conception he applied to the interpretation of the ammonio-cobalt bases, and so, too, did Blomstrand two years later. If we consider theories of this kind, not as finalities, but as attempts

to express known relations in symbolic forms, we must admit that Gibbs's conception was useful, and served well for the time being. That it has given way to other views more in harmony with modern discoveries, is not at all to the discredit of its author. In the later papers by Gibbs, published in 1875 and 1876, he made good use of his hypotheses, and described many more ammonio-cobalt compounds. Among them were the salts of an entirely new base, croceocobalt, in which two nitro-groups were present. In all, five distinct series were studied, their chlorides being represented, in modern notation, by the subjoined formulæ:

Luteocobalt chloride,	$Co(NH_3)_6Cl_3$.
Roseocobalt chloride,	$Co(NH_3)_5 \cdot H_2O \cdot Cl_3$.
Purpureocobalt chloride,	$Co(NH_3)_5 \cdot Cl \cdot Cl_2$.
Xanthocobalt chloride,	$Co(NH_3)_5 \cdot NO_2 \cdot Cl_2$.
Croceocobalt chloride,	$Co(NH_3)_4(NO_2)_2 \cdot Cl$.

Gibbs's formulæ were somewhat different from these, being doubled, and with the water of roseocobalt regarded not as constitutional, but as crystalline. The simpler, halved expressions were established by cryoscopic methods which did not exist when Gibbs conducted his investigations.

The researches on the platinum metals, published by Gibbs in the years 1861 to 1864, relate mainly to analytical methods. Processes for the solution of iridosmine were carefully studied, and various new separations of the several metals from one another were devised. Incidentally, a number of new compounds were prepared, which, with a few exceptions, Gibbs never fully described. In 1871, however, he published a brief note on the remarkable complex nitrites formed by iridium, and in 1881 he described a new base, osmyl-ditetramine, $OsO_2,4NH_3$, together with several of its salts. These researches were never pushed very far, and were discontinued for lack of proper facilities. They were, nevertheless, distinct additions to our knowledge of the platinum group.

I have already mentioned the work done by Gibbs and his students in the laboratory of the Lawrence Scientific School. This covered a wide range, partly in developing and perfecting old analytical methods, partly in devising new ones. There were improvements in gas analysis, especially in the determination of nitrogen, and a great variety of analytical separations. I will not attempt to give a catalogue of these investigations, but will limit myself to a few of the more noteworthy. A new volumetric method for analysing the salts of heavy metals was worked out, in which a metal such as copper or lead was precipitated as sulphide, the acid being afterwards determined by titration. The estimation of

manganese as pyrophosphate was another of these contributions to analysis. But the most important of all was the electrolytic determination of copper, now universally used, which was first published from Gibbs's laboratory. It is true that a German chemist, Luckow, claimed to have used the method much earlier, but so far as I can discover he failed to publish it. Gibbs, therefore, is entitled to full credit for a process which was the progenitor of many others. The entire field of electrochemical analysis was thrown open by him, and it has been most profitably cultivated. Gibbs also, during this period of his activity, invented several instrumental devices of great convenience. The ring burner, and the use of porous septa when precipitates are to be heated in gases, are due to him. Furthermore, in co-operation with E. R. Taylor, he devised a glass and sand filter which was the forerunner of the porous cones invented by Munroe when the latter was a student in Gibbs's laboratory. That, in turn, preceded the well-known perforated crucibles of Gooch, who was one of Gibbs's assistants. The genealogy of these inventions is perfectly clear.

We come now to the remarkable series of researches on the complex inorganic acids, which Gibbs began to publish in 1877, and continued well into the 'nineties. The ground had already been broken by others; silicotungstates, phosphotungstates, phosphomolybdates, etc., were fairly well known, but they were commonly regarded as exceptional compounds rather than as representatives of a very general class. In his first, preliminary, communication upon the subject, Gibbs indicated the vastness of the field to be explored, and showed that the formation of complex acids was characteristic of tungsten and molybdenum to an extraordinary degree. The phenomena were general, not special; and no limit could be assigned to the possible number of acids which these elements might form.

In his systematic work, following his preliminary announcement, Gibbs first revised the sodium tungstates in order to determine their true composition. Then, after preparing a number of phosphotungstates and phosphomolybdates, he studied the corresponding compounds containing arsenic in place of phosphorus. He next obtained similar vanadium compounds, and also showed that the phosphoric oxide of the first known acids was replaceable by phosphorous and hypophosphorous groups. Later still, he replaced the normal phosphates by pyro- and meta-phosphates, and also prepared complex salts containing arsenious, antimonious, and antimonic radicles. Stanno-phosphotungstates and molybdates, platinotungstates, and complex acids containing mixed groups were discovered, together with analogous compounds of selenium,

tellurium, cerium, and uranium. One salt described, a phospho-vanadio-vanadico-tungstate of barium, had the formula

$$60WO_3,3P_2O_5,V_2O_5,VO_2,18BaO,150H_2O,$$

with a molecular weight of 20066. Compared with this substance, the supposed complexity of most organic compounds becomes simplicity itself, and their interpretation seems relatively like child's play. In all, Gibbs described complex salts belonging to more than fifty distinct series, and did his work in a small private laboratory with only a single assistant. With greater resources at his command, what might he not have accomplished?

In 1898, in his address as retiring president of the American Association for the Advancement of Science, Gibbs summed up his views as to the constitution of the complex acids. His presentation of the subject, however, can hardly be regarded as final. The problems involved are too complicated to be easily solved, and much future investigation is needed in order to determine the true character of these extraordinary substances. Gibbs was a pioneer, breaking pathways into a tangled wilderness; but the ways are now open, and he who wills may follow. Possibly some of the compounds so far obtained were double salts; others may have been isomorphous mixtures; and in some instances phenomena of solid solution perhaps obscured the truth. By physical methods, cryoscopic or ebullioscopic, the molecular weights of the salts must be determined; their ionisation needs to be studied, and in such ways their true nature can be ascertained. These methods of research have been mainly developed since the work of Gibbs was done; he, therefore, cannot be criticised for not employing them. Since his time chemists have come to recognise many compounds as salts containing complex ions, such as, for example, the oxalates, tartrates, etc., of iron, aluminium, chromium, and antimony with other bases of lower valency. Even many of the silicates are easiest to interpret as salts of alumino-silicic acids, although the physical proof of their nature is difficult to obtain. The constitution of the complex acids is one of the great outstanding problems of inorganic chemistry.

Although he was distinctively an inorganic chemist, Gibbs did not entirely neglect organic chemistry. In 1868 he discussed the constitution of uric acid and its derivatives, and in 1869 he described some products formed by the action of alkali nitrites on them. He also produced several memoirs on optical subjects, such as one on a normal map of the solar spectrum, and another on the wave-lengths of the elementary spectral lines. Again, he devoted some time to the study of interference phenomena, and discovered a constant, which he called the interferential constant,

that was independent of temperature. One of Gibbs's latest papers, published when he was seventy-one years old, related to that extremely difficult subject, the separation of the rare earths, a subject in which he had always taken a deep interest. In this paper he developed a new method for determining the atomic weights of the rare-earth metals, which was based upon analyses of their oxalates. The oxalic acid was determined by titration with permanganate solutions, and the oxides by ignition of the salts. From the ratios between the oxalic acid and the oxides, the molecular weights of the latter could be computed without reference to the amount of moisture in the initial substances. This method has since been employed by others, and especially by Brauner, in his work on the atomic weights of cerium and lanthanum. It is worth noting here that Gibbs had previously taken some part in atomic weight determinations. Those of Wing on cerium, and of Lee on cobalt and nickel, were made in Gibbs's laboratory and under his guidance. Furthermore, Gibbs was one of the earliest American chemists, if not the first, to accept the modern or Cannizzaro system of atomic weights, and to use it in his teaching. His mind was never closed to new ideas. It welcomed light from all sources.

Gibbs wrote no books and delivered no popular lectures. He was therefore little known to the public at large, but within scientific circles he received high honours. He was one of the founders of the National Academy of Sciences, and at one time its President, and he also presided over the American Association for the Advancement of Science. Honorary membership in the German, English, and American chemical societies, and in the Prussian Academy, was conferred upon him, and he received honorary degrees from several universities. His life was that of a devoted scholar, caring most for research, and indifferent to popularity. Sensationalism and self-advertising were most obnoxious to him; indeed, in these respects, no man could be more fastidious. The approval of his fellows he fully appreciated, but only when it was spontaneous and deserved. It must not be inferred from these remarks that Gibbs was deficient in public spirit, for that would be most untrue. During the Civil War, from 1861 to 1865, he was strongly patriotic, and did much to help the Union side. The Union League Club of New York, organised to bring together the more patriotic citizens of that city, was founded at a meeting in his house, and is to-day a strong social institution. Gibbs was also active in the Sanitary Commission, an organisation modelled upon the work of Florence Nightingale in the Crimea, and the forerunner of the Red Cross Society of to-day.

Wolcott Gibbs was a man of striking personality, tall, erect, and

dignified. As with most men of positive character, he had strong likes and dislikes, but the latter never assumed unworthy form. To his friends he was warmly devoted, and always ready to help them in their work with manifold suggestions. His breadth of mind is indicated by the range of his researches, and his liberality by the way in which he encouraged his students to develop his ideas. More than one important investigation was based upon hints received from him, and was carried out under his supervision, to appear later under another name. Gibbs never absorbed the credit due even in part to others, nor failed to recognise the merits of his assistants in the fullest way. Had he been more selfish, his list of publications would have lengthened; but his sense of justice was most keen, and therefore he held the esteem and confidence of his co-workers. No man, not even among his opponents, for such there were, could ever accuse him of unfairness. He deserved all honour, and his name will live long in the history of that science to which his life was given.

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ФОТОТИПІЯ А. Ф. ДРЕССЛЕРА, СПБ.

Д. Менделеевъ

MENDELÉEFF MEMORIAL LECTURE.

Delivered on October 21st, 1909.

By W. A. Tilden, D.Sc., LL.D., F.R.S., Past-President of the Chemical Society.

To many of the present generation of English chemists, the commanding, patriarchal figure of Mendeléeff was quite familiar. Though his several visits to London were often connected with official business of the Russian Government Department of Weights and Measures, of which he was the chief official during the later years of his life, he came several times with more purely scientific objects. In 1889 the occasion of his presence in London was the Faraday Lecture which he had been invited to give to the Chemical Society, but which, owing to a sudden and urgent recall to his home, he was unable to deliver in person. His last appearance in this country was in November, 1905, when the Copley Medal was awarded to him by the Royal Society.

The Chemical Society can see his face no more, and all that it can now do is to inscribe high on its roll of honour the name which, more than any other, will be for ever associated with the development of the great generalisation known as the periodic system of the elements.

Dmitri Ivanovitsch Mendeléeff * was the fourteenth and youngest child of his parents, Ivan Pavlovitsch and Maria Dmitrievna, *née* Kornileff. His father, a former student of the Chief Pedagogic Institute of St. Petersburg, obtained the appointment of Director of the Gymnasium at Tobolsk, in Siberia, where he met Maria Dmitrievna, who became his wife. After a few years at Tobolsk, he was transferred to school directorships in Russia, first at Tambov, and afterwards at Saratov. But in order to satisfy the ardent wish of his wife, he took advantage of an opportunity of exchange, by which he became once more Director of the College at Tobolsk, and the family returned to Siberia. Here on January 27th, 1834 (O.S.) was born Dmitri Ivanovitsch, the youngest son.

* For many of the details of Mendeléeff's career and of his home life the writer is indebted to the family chronicle compiled, soon after his death, by his niece, N. J. Gubkina (*née* Kapustina), and published in St. Petersburg, also to pamphlets by A. Archangelsky and P. J. Robinowitsch. He also desires to express his thanks to Mr. D. V. Jéquier, of St. Petersburg, as well as to several Russian friends, for valuable assistance in translation.

Soon after his birth the father became gradually blind from cataract in both eyes, and was obliged to resign, the whole family, including eight children, having to subsist on a small pension of 1000 roubles (about £100 per annum). The mother, Maria Dmitrievna, belonged to the old Russian family, Kornileff, settled at Tobolsk. They were the first to establish in Siberia the manufacture of paper and glass. In 1787 the grandfather of Dmitri opened at Tobolsk the first printing press, and from 1789 produced the first newspaper in Siberia, the *Irtysch*. The glass works were situated in the village of Aremziansk, a short distance from Tobolsk.

According to the family tradition, one of the Kornileffs in a previous generation had married a Khirgis Tartar beauty, whom he loved so passionately that when she died he also died of grief. The pure Russian blood thus received a strain of the Mongolian race, and some of their descendants preserved traces of the Oriental type. This, however, was not very noticeable in the features of the chemist.

From her childhood, Maria Dmitrievna was distinguished by her intelligent wish for instruction, and having no other resource when her brother Basile went to school she repeated by herself all his lessons, and thus, unaided, obtained some part of the knowledge so eagerly desired. There can be no doubt she was a woman possessed of remarkable vigour of mind, who exercised great influence over her children. Her activity and capacity are further illustrated by the fact that when her husband became blind she revived the business of the glass works, and carried it on till after his death from consumption in 1847.

Tobolsk was at that time a place of banishment for many political exiles, the so-called Decembrists, one of whom, Bassargin, married Olga, an elder sister of Dmitri. To these Decembrists the boy owed his first interest in natural science. His mother had always cherished the hope that at least one of her children would devote himself to science, and accordingly, after her husband's death and the destruction of the glass works by fire, and spite of failing health and scanty means, she undertook the long and tedious journey from Tobolsk to Moscow, accompanied by her remaining children, Elizabeth and Dmitri Ivanovitsch, with the object of entering the latter, then nearly fifteen years of age, at the University. Disappointed in this object, owing to official difficulties, she removed in the spring of 1850 to St. Petersburg, where ultimately, with the assistance of the Director, Pletnoff, of the Central Pedagogic Institute, a friend of her late husband, she succeeded in securing for her son admission to the Physico-

Mathematical Faculty of the Institute, together with much-needed pecuniary assistance from the Government.

The debt which Dmitri Ivanovitsch owed to his mother he acknowledged later in the introduction to his work on "Solutions," which he dedicated to her memory in the following interesting lines:

"This investigation is dedicated to the memory of a mother by her youngest offspring. Conducting a factory, she could educate him only by her own work. She instructed by example, corrected with love, and in order to devote him to science she left Siberia with him, spending thus her last resources and strength. When dying, she said, 'Refrain from illusions, insist on work, and not on words. Patiently search divine and scientific truth.' She understood how often dialectical methods deceive, how much there is still to be learned, and how, with the aid of science without violence, with love but firmness, all superstition, untruth, and error are removed, bringing in their stead the safety of discovered truth, freedom for further development, general welfare, and inward happiness. Dmitri Mendeléeff regards as sacred a mother's dying words. October, 1887."

In the Pedagogic Institute Dmitri Ivanovitsch was thus able to devote himself to the mathematical and physical sciences under the guidance of Professors Leng and Kupfer in physics, Woskresensky in chemistry, and Ostragradsky in mathematics. Unfortunately, at the end of his course, his health failed, and about this time his mother died. Having been ordered to the South, he fortunately obtained an appointment as chief science master at Simferopol, in the Crimea. The southern climate soon alleviated the serious symptoms of lung disorder, and removal being necessary in consequence of the Crimean War, he was able soon afterwards to undertake a post as teacher of mathematics and physics at the Gymnasium at Odessa. In 1856 he returned to St. Petersburg, and at the early age of twenty-two he was appointed *privat docent* in the University, having secured his certificate as master in chemistry.

At this time he appears to have passed rapidly from one subject to another, but he soon found matter for serious and protracted study in the physical properties of liquids, especially in their expansion by heat. And when, in 1859, by permission of the Minister of Public Instruction Mendeléeff proceeded to study under Regnault in Paris and afterwards in Heidelberg, he devoted himself to this work, communicating his results to Liebig's *Annalen* and the French Academy of Sciences. Returning two years later to St. Petersburg, he secured his Doctorate, and was soon after-

wards appointed Professor of Chemistry in the Technological Institute. In 1866 he became Professor of General Chemistry in the University, Butlerow at the same time occupying the Chair of Organic Chemistry.

As a teacher, Mendeléeff seems to have possessed a special talent for rousing a desire for knowledge, and his lecture room was often filled with students from all faculties of the University. Many of his former students remember gratefully the influence he exercised over them.* One of these writes: "I was a student in the Technological Institute from 1867 to 1869. Mendeléeff was our professor, and in 1868 taught organic chemistry. The previous course by the professor of inorganic chemistry consisted of a collection of recipes, very hard to remember, but, thanks to Mendeléeff, I began to perceive that chemistry was really a science. The most remarkable thing at his lectures was that the mind of his audience worked with his, foreseeing the conclusions he might arrive at, and feeling happy when he did reach these conclusions. More than once he said, 'I do not wish to cram you with facts, but I want you to be able to read chemical treatises and other literature, to be able to analyse them, and, in fact, to understand chemistry. And you should remember that hypotheses are not theories. By a theory I mean a conclusion drawn from the accumulated facts we now possess which enables us to foresee new facts which we do not yet know.' He was considered among the students a most liberal man, and they thought of him as a comrade. More than once during a disturbance between the students and the administration Mendeléeff supported the students, and under his influence many matters were put right." (L. G.) Another former student in the University writes as follows: "I am sorry to say I did not know Mendeléeff personally. I only had the good fortune to follow, in the years 1867-69, his lectures on both Organic and Inorganic Chemistry. The former was an abridged course, which he had the admirable idea to deliver for us students of the mathematical branch of the physico-mathematical faculty. He reduced this course of one lecture a week during one year to a general review of organic compounds and the general laws of their structure. You can imagine what it must have been in the hands of Mendeléeff, thirty-three or thirty-four years old at that time, in the full enjoyment of his mental powers, and just then plunged into the study of his great generalisations. For me it was a revelation, being occupied with the great questions connected with the development of the new system of atomic weights,

* For the following reminiscences, the writer is indebted to Mr. L. Goldenberg and Prince P. Kropotkin respectively.

the mechanical theory of heat, etc. Grove's, Thomson's, Joule's, Séguin's works were then just out, and in these years a sudden blossoming of the natural sciences in all directions seemed to bring us near to the solution of the great problems of the nature of matter and of gravitation. Then I followed Mendeléeff's lectures on Inorganic Chemistry. The 'Principles of Chemistry' was not yet out, but he was evidently writing it at that time. You know how much is said in the footnotes to his 'Principles'; well, imagine each of these notes developed into a beautiful improvisation, with all the freshness of thought of a man who, while he speaks, evolves all the arguments for and against, there on the spot. The hall was always crowded with something like two hundred students, many of whom, I am afraid, could not follow Mendeléeff, but for the few of us who could it was a stimulant to the intellect and a lesson in scientific thinking which must have left deep traces in their development, as it did in mine." (P. K.)

One of Mendeléeff's most remarkable personal features was his flowing abundance of hair. The story goes that, before he was presented to the late Emperor, Alexander III., his Majesty was curious to know whether the professor would have his hair cut. This, however, was not done, and he appeared at Court without passing under the hands of the barber. His habit was to cut his hair once a year in spring, before the warm weather set in. His eyes, though rather deep set, were bright blue, and to the end of his life retained their penetrating glance. Tall in stature, though with slightly stooping shoulders, his hands noticeable for their fine form and expressive gestures, the whole figure proclaimed the grand Russian of the province of Tver.

At home, Mendeléeff always wore an easy garment of his own design, something like a Norfolk jacket without a belt, of dark grey cloth. He rarely wore uniform or evening coat, and attached no importance to ribbons and decorations, of which he had many.

As to his views on social and political questions, many people thought him a rigid monarchist, but he said of himself that he was an evolutionist of peaceable type, desiring a new religion, of which the characteristic should be subordination of the individual to the general good. He always viewed with much sympathy what is called the feminine question. At the Office of Weights and Measures, he employed several ladies, and about 1870 he gave lectures on chemistry to classes of ladies. Nevertheless he considered women inferior to men both in business and in intellectual pursuits, and he thought the chief promoters of the feminine movement aimed, not so much at equality of political position, as at opportunities for work and to escape inactivity. But he thought

the feminine temperament specially suited to all branches of art in the broadest sense of the word, including education.

Mendeléeff held decided views on the subject of education, which he set forth in several publications, especially "Remarks on Public Instruction in Russia" (1901). Here he says, "The fundamental direction of Russian education should be living and real, not based on dead languages, grammatical rules, and dialectical discussions, which, without experimental control, bring self-deceit, illusion, presumption, and selfishness." Believing in the soothing effect of a vital realism in schools, he considered that universal peace and the brotherhood of nations could only be brought about by the operation of this principle. Speaking of the reforms desirable, he says that "for such reforms are required many strong realists; classicists are only fit to be landowners, capitalists, civil servants, men of letters critics, describing and discussing, but helping only indirectly the cause of popular needs. We could live at the present day without a Plato, but a double number of Newtons is required to discover the secrets of nature, and to bring life into harmony with the laws of nature." Mendeléeff was evidently a philosopher of the same type as our own Francis Bacon.

"I am not afraid," he says later, "of the admission of foreign, even of socialistic, ideas into Russia, because I have faith in the Russian people, who have already got rid of the Tartar domination and the feudal system."

Mendeléeff always dined at six o'clock, and liked to entertain his friends and relations, but in his own diet he was extremely moderate. After dinner he enjoyed reading light literature, especially books of adventure, such as those of Fenimore Cooper or Jules Verne. But his literary tastes were peculiar. Though interested in serious literature and appreciating Shakespeare, Schiller, Goethe, Victor Hugo, and Byron as well as the Russian classics, beginning with Zhoucovsky and Pouschkin, his favourites among Russian poets were Maïcoff and Tuttcheff, and among the rest Byron. Of the last-named he preferred to all his other works the gloomy poem called "Darkness," and among the rest the "Silentium" of Tuttcheff.

He rarely went to the theatre, and did not approve of frequent visits to the theatre by his children, as he considered such distractions tend to destroy concentration and fill the mind with "trifles and foolishness." On the other hand, he was very fond of pictures, and he visited all the exhibitions. That he was interested in questions relating to art, and had given much thought to æsthetic problems, is indicated by a letter * which he addressed in November, 1880, to the well-known Russian daily paper of that time,

* Considerably condensed in the following abstract.

Goloss (*The Voice*), on the subject of a picture by Kouindji, "Night in the Ukraine." Writing of the influence of landscape on different minds, he says, "At first it seemed to me a matter of personal taste, of individual sensitiveness of different persons to the beauty of nature." But, rejecting this simple view, he was led to a conception which he regarded as really satisfactory, and which he wished to share with others. He says, "Landscape was depicted in antiquity, but was not in favour in those times. Even the great masters of the sixteenth century made use of it merely as a frame to their pictures. It was the human form which principally inspired artists of that epoch; even the gods and the Almighty Himself appeared to their minds in human shape. In this alone they found the infinite, the inspiring, the divine. And this was because they worshipped human mind and human spirit. This found expression in science in an exceptional development of mathematics, logic, metaphysics, and politics. Later, however, men lost faith in the absolute and original power of human reason, and they discovered that the study of external nature assists even in the correct appreciation of the nature of the human inner self. Thus nature became an object of study; a natural science arose unknown either to antiquity or to the period of the Renaissance. Observation and experience, inductive reasoning, submission to the inevitable, soon gave rise to a new and more powerful, more productive method of seeking truth. It thus became evident that human nature, including its consciousness and reason, is merely a part of the whole, which is easier to comprehend as such from the study of external nature than of the inner man. External nature thus ceased to be merely subservient to man, and became his equal, his friend. Dead and senseless as it had been, it now became alive. Everywhere it presented motion, stores of energy, natural reason, simplicity, and plan. Inductive and experimental science became a crown of knowledge, royal metaphysics and mathematics had now to be content with modest questioning of nature. Landscape painting was born simultaneously with this change, or perhaps a little earlier. Thus it will probably come to pass that our age will hereafter be known as the epoch of natural science in philosophy, and of landscape in art. Both derive their materials from sources external to man. . . . Man has, however, not been lost sight of as an object of study and of artistic creation, but he now appears, not as a potentate or as a microcosm, but merely as part of a complex whole."

In 1863, when twenty-nine years of age, Mendeléeff married his first wife, *née* Lestshoff, by whom he had one son, Vladimir,* and a daughter, Olga; but the marriage proved unhappy, and after

* Died in 1899, aged 34.

living apart for some time there was a divorce. In 1877 he fell in love with a young lady artist, Anna Ivanovna Popova, of Cossack origin, and in 1881 they were married. This lady exercised considerable influence over his views about art, and the walls of his study were furnished with many products of her pencil, notably portraits of Lavoisier, Descartes, Newton, Galileo, Copernicus, Graham, Mitscherlich, Rose, Chevreul, Faraday, Berthelot, and Dumas, and others of relatives. After his second marriage, Mendeléeff lived first at the University, and afterwards in the apartments built for the Director at the Bureau of Weights and Measures, and here his younger children were born, Lioubov (Aimée), Ivan (Jean), and the twins, Maria and Vassili (Basile).

In 1890, in consequence of a difference with the administration, Mendeléeff retired from the Professorship in the University. During the disturbances among the students in that year, he succeeded in pacifying them by promising to present their petition to the Minister of Education. Instead of thanks for this service, however, the Professor received a sharp reprimand from the authorities for not minding his own business. The consequence was that Mendeléeff resigned. Independently of the petition, however, there were probably deeper reasons for his being out of favour with the Ministry, connected with his irreconcilable enmity to the classical system of education already referred to (p. 130). Of this he had made no secret, and it had already brought him into conflict with the authorities. In 1893, however, he was appointed by M. Witte to the office of Director of the Bureau of Weights and Measures, which he retained till his death.

In the earlier part of his life, Mendeléeff was interested in carrying on a series of agricultural experiments on his Tver estate, Boblovo. The peasants, much struck by his success and the abundance of his crops, inquired of him whether this was due to his luck or to his "talent." With a smile and the patois which he always affected in speaking to the country people, he informed them that he certainly had "talent," and, as he said afterwards at home, there is no merit in having luck.

Once during the solar eclipse in 1887 he ascended alone in a balloon wih the object of making scientific observations. His assistant, Kovanko, who sat with him in the basket, alighted at the last moment, probably ordered to do so by his chief because the balloon would not rise. When the balloon shot up quickly and disappeared in the clouds, his family was naturally very much alarmed. Fortunately the hero of the adventure was able to descend safely, and a few hours later returned to his family from Moscow. The peasant women thereafter used to tell that Dmitri

Ivanovitsch flew on a bubble and pierced the sky, and for this the authorities made him a chemist!

Mendeléeff was very democratic in his habits, and when travelling from the Capital to his estate, six or seven hours by rail, he always made use of the third class, and on the way talked freely to his fellow-passengers on all sorts of subjects, so that at the end of the journey he was surrounded by all sorts of people. At the railway station, about twelve miles from Boblovo, he was always met by the same driver, Zassorin, who with his troika of greys transported the whole family at full gallop, according to Russian custom.

Such, then, are the chief features of a great personality. If it be admitted that stories are told of his occasional irritability of temper, we can well place on the other side of the account the cordial relations always subsisting between the Professor and his assistants, the confidence and respect between the Master and his servants, the deep affection between the Father and his children, which are known to have persisted throughout his life, and which could be illustrated by many anecdotes. These stories merely serve "to give the world assurance of a man."

For us who live on the other side of Europe, separated as we are by race, by language, by national and social customs, and by form of government, it is not easy to understand completely the texture of such a mind, the quality of such genius, and the conditions, social or political, which may have served to encourage or to repress its activity. The Russian language may be eloquent, expressive, versatile, and harmonious, or it may possess any other good quality that may be claimed for it by those to whom it is a mother tongue, but the fact remains that it is a barrier to free intercourse between the Russian people and the world outside the Russian Empire. This alone creates a condition which must influence the development of thought, and must give to Russian science and philosophy a colour of its own. Mendeléeff was, like many educated Russians, a man of very liberal views on such subjects as education, the position of women, on art and science, and probably on national government. We can hardly guess what would be the influence on such a nature of a rigid administrative *régime* which forbids even the discussion of such questions. We in England are almost unable to imagine such a state of things as would be represented by the closing of, say, University College for a year or more, because the question whether the House of Lords ought to be abolished had been debated in the Students' Union. Imagine the Professor of Chemistry, along with his colleagues, for such a reason deprived of the use of his laboratory

by the police, and only allowed to resume his studies when someone down at Scotland Yard thought proper. Such being the experience of most of the Russian Universities and Technical High Schools, it is not surprising that the output of Russian science, notwithstanding the acknowledged genius of the Russian people, appears sometimes comparatively small. The amount of work done by Mendeléeff, both experimental and theoretical, was prodigious, and all the more remarkable considering the cloudy atmosphere under which so much of it was accomplished.*

In 1882 the Royal Society conferred on Mendeléeff, jointly with Lothar Meyer, the Davy Medal. In 1883 the Chemical Society elected him an Honorary Member, and in 1889 it conferred upon him the highest distinction in its power to award, namely, the Faraday Lectureship, with which is associated the Faraday Medal. In 1890 he was elected a Foreign Member of the Royal Society, and in 1905 he received the Copley Medal. So far as England is concerned, his services to science received full acknowledgment. It is all the more remarkable, therefore, that he never became a member of the Imperial Academy of Sciences of St. Petersburg.

Towards the end of 1906 Mendeléeff's health began to fail. Nevertheless he was able to attend the Minister on the occasion of an official visit in January to the office of Weights and Measures, but he caught cold and, enfeebled as he had been by influenza in the preceding autumn, inflammation of the lungs set in. Retaining consciousness almost to the last, he requested even on the day of his death to be read to from the "Journey to the North Pole," by his favourite author, Jules Verne. He died in the early morning of the 20th January (O.S.), 1907, within a few days of his seventy-third birthday. He was buried in the Wolkowo Cemetery beside the graves of his mother and son.

Turning now to a survey of Mendeléeff's work as a man of science, it will be sufficient if we pass lightly over his first essays. Like so many other chemists, he began by handling simple questions of fact, his first paper, dated 1854, when he was twenty years of age, being on the composition of certain specimens of orthite. It was not till 1859 that he settled down to serious examination of the physical properties of liquids, which led him to a long series of experiments on the thermal dilatation of liquids, of which the

* Professor Walden, at the end of a biographical notice recently published in the *Berichte d. Deut. Chem. Ges.*, April, 1909, gives a list of 262 printed publications by Mendeléeff. These include, not only memoirs on physical and chemical subjects, but books, pamphlets, reports, and newspaper articles relating to exhibitions, to the industries of Russia, to weights and measures, to education, to art, and even to spiritualism.

chief ultimate outcome was the establishment of a simple expression for the expansion of liquids between 0° and the boiling point (Trans., 1883, **45**, 126). This formula is liable to the same kind of modification which has been found necessary in the case of gases. It is, of course, applicable only to an ideal liquid from which all known liquids differ by reason of differences of chemical constitution and consequent differences of density, viscosity, and other properties. Thorpe and Rücker, by applying van der Waals' theory of the general relation between the pressure, volume, and temperature of bodies to Mendeléeff's expression for the thermal expansion, developed a simple method of calculating the critical temperature of liquids from observations of their expansion (Trans., 1884, **45**, 135).

Mendeléeff devoted a large amount of time and of experimental skill to the estimation of the densities of various solutions, especially mixtures of alcohol and water and of sulphuric acid and water, and of aqueous solutions of a large number of salts. In 1889 he embodied the whole in the monograph already referred to. In a paper communicated to the Transactions in 1887 (**51**, 779), he stated his views in the following words: "Solutions may be regarded as strictly definite atomic chemical combinations at temperatures higher than their dissociation temperatures. Definite chemical substances may be either formed or decomposed at temperatures which are higher than those at which dissociation commences; the same phenomenon occurs in solutions; at ordinary temperatures they can be either formed or decomposed." This view was retained by Mendeléeff, and appears in a footnote (p. 64) in the 7th Russian Edition (3rd English Edition) of the *Principles*, 1902, where the following passage occurs: "The conception of solutions as dissociated definite liquid chemical compounds is based on the following considerations: (1) That there exist certain undoubtedly definite crystallised chemical compounds (such as H_2SO_4,H_2O, or $NaCl.2H_2O$, or $CaCl_2,6H_2O$, etc.), which melt on a certain rise of temperature and then form true solutions; (2) that metallic alloys in a molten condition are real solutions, but on cooling they often give entirely distinct and definite crystallised compounds; (3) that between the solvent and the substance dissolved there are formed in a number of cases many undoubtedly definite compounds, such as compounds with water of crystallisation; (4) that the physical properties of solutions, and especially their specific gravities (a property which can be very accurately determined), vary with a change in composition, and in such a manner as would be required by the formation of one or more definite but dissociating compounds. . . . The increase in specific

gravity (ds) varies in all well-known solutions with the proportion of substance dissolved (dp), and this dependence can be expressed by a formula $ds/dp = A + Bp$ between the limits of definite compounds, whose existence in solutions must be admitted." Applying this method, he concludes that mixtures of alcohol and water may contain several definite compounds, such as $C_2H_6O + 3H_2O$. These views, however, did not prevent his recognising van't Hoff's gas theory as applicable to dilute solutions.

In conjunction with some of his students, Mendeléeff also studied minutely the question of the elasticity of gases, and published several papers on the subject (see Royal Soc. Catalogue), extending over a period of some ten years from 1872. From the earlier researches of Regnault and others, it was known that the law of Boyle and Marriotte is not strictly applicable either to all gases or at all pressures. Mendeléeff and his assistants devoted special attention to the departures from the theoretical requirements of the law exhibited by gases under very greatly reduced pressures. He found that for hydrogen the value of pv diminishes with the pressure down to 20 mm., while for air, carbon dioxide, and some others, pv increases slightly to a maximum.

Another subject to which Mendeléeff gave a good deal of attention was the nature and origin of petroleum. Having already reported in 1866 on the naphtha springs in the Caucasus, in the summer of 1876 he crossed the Atlantic and surveyed the oil fields of Pennsylvania. In the course of these investigations, he was led to form a new theory of the mode of production of these natural deposits. The assumption that the oil is a product of the decomposition of organic remains he rejects on a variety of grounds, which are set forth in a communication to the Russian Chemical Society (Abstract, see *Ber.*, 1877, **10**, 229). Mendeléeff assumes, as others have done, that the interior of the earth consists largely of carbides of metals, especially iron, and that hydrocarbons result from the penetration of water into contact with these compounds, metallic oxide being formed simultaneously. The hydrocarbons are supposed to be driven in vapour from the lower strata, where temperature is high, to more superficial strata, where they condense and are retained under pressure. In 1886, in consequence of rumours as to the possible exhaustion of the Russian oil fields, he was sent by the Government to Baku to collect information, and in 1889 he made a communication on this subject to Dr. Ludwig Mond, which is printed in the Journal of the Society of Chemical Industry (1889, **8**, 753.)

The influence of the great generalisation known as the periodic law can best be estimated by reviewing the state of knowledge

and opinion before the announcement and acceptance of the principle by the chemical world, and subsequently glancing at the influence which, directly or indirectly, it has produced on scientific thought, not only in regard to the great problems to which it immediately relates, but to the whole range of chemical theory.

The use of the expression, "atomic weight," implies the adoption of some form of atomic theory. But forty or more years ago Dalton's atomic theory was by many of the most philosophical chemists and physicists regarded as only a convenient hypothesis, which might be temporarily useful, but could not be accepted as representing physical reality. Since that time, however, a variety of circumstances have contributed to consolidate the Daltonian doctrine. The estimation of the ratios called atomic weights has been the subject of research, attended by more and more elaborate precautions to secure accuracy, from the time of Dalton himself onward through successive generations down to the present day. Though the atomic weights of the majority of the common elements are now known to a high degree of accuracy, the acknowledged errors have been sufficiently great to render abortive various attempts to reduce them to any common scheme of mathematical relationship. As is well known, the most important step toward the systematisation of atomic weights was taken about 1860, mainly on the grounds eloquently and convincingly set forth by Cannizzaro,* in consequence of which the arbitrary selection of numbers for atomic weights was superseded by the practical recognition of the law of Avogadro and the application of the law of Dulong and Petit, so that a common standard was established. No general scheme of atomic weights was previously possible, partial and imperfect efforts in this direction being represented by Dœbereiner's triads and the principle of homology made use of by Dumas. Only so soon as numbers representing the atomic weights of calcium, barium, lead, and other metals were corrected and brought into the same category as those of oxygen, sulphur, and carbon was there some chance of determining whether these numbers possessed a common factor or were capable of exhibiting mathematical interrelations which might be regarded as symbolic of physical relations or even directly dependent upon them. The first step in this direction was taken by J. A. R. Newlands, who, after some preliminary attempts in 1864-1865, discovered that when the elements are placed in the order of the numerical value of their atomic weights, corrected as advised by Cannizzaro, the eighth element starting from any point on the list exhibits a revival of the characteristics of the first. This undoubtedly repre-

* 1858, and later, Faraday Lecture, 1872.

sents the first recognition of the principle of periodicity in the series of atomic weights, but whether discouraged by the cool reception of his "law of octaves" by the chemical world or from imperfect apprehension of the importance of this discovery, Newlands failed to follow up the inquiry. It was not long, however, before the matter was taken up by others, and doubtless the improvements in the estimation of atomic weights, following on the work of Stas, then only recently published, inspired greater confidence in the approximate accuracy of the numbers adopted as atomic weights, and thus encouraged inquiry into their relations. The subject is, indeed, an attractive one, for it involves considerations which lie at the foundations of all our notions respecting the physical constitution of matter, and accordingly we find papers by many chemists dealing with the question of these numerical relations. Odling especially seems to have given much thought to the subject, and, ignoring Newlands' previous attempts, he drew up towards the end of 1864 * a table containing a list of all the then well-known elements, arranged horizontally in the order of their generally accepted groups, and perpendicularly in the order of their several atomic weights. He concludes an article in Watts's Dictionary a few months later with these words: "Doubtless some of the arithmetical relations exemplified in the foregoing table are merely accidental, but, taken altogether, they are too numerous and decided not to depend on some *hitherto unrecognised* law." It is important to note the words I have italicised.

Such, then, was the state of knowledge about this time. Evidently the way was being prepared, but the prophet had not made his appearance, the seer who could look with the eyes of confidence beyond the clouds of uncertainty which obscured all ordinary vision.

In March, 1869, Mendeléeff communicated to the Russian Chemical Society an enunciation of the principle of periodicity and a statement of some of the consequences of this recognition of the relation of properties to atomic weight throughout the whole range of the known elements, and this statement was accompanied by a table which, while it bears a close resemblance to Odling's table of 1864, was apparently connected in his mind with an idea which became clearer and more decisive in the modifications which he immediately afterwards introduced into the arrangement.†

* *Quart. J. Sci.*, 1864, **1**, 643; and Watts' Dict., Vol. III, 975.

† Subjoined is a translation, as literal as possible, of the German Abstract (*Zeitsch. f. Chem.*, **5**, 405). Several obvious misprints have been corrected.

On the Relation of the Properties to the Atomic Weights of the Elements.

By D. MENDELÉEFF.

When the elements are arranged in vertical columns, according to increasing atomic weight, so that the horizontal lines contain analogous elements, again according to increasing atomic weight, the following arrangement results, from which several general conclusions may be derived:

			Ti = 50	Zr = 90	? = 180	
			V = 51	Nb = 94	Ta = 182	
			Cr = 52	Mo = 96	W = 186	
			Mn = 55	Rh = 104·4	Pt = 197·4	
			Fe = 56	Ru = 104·4	Ir = 198	
			Ni = Co = 59	Pd = 106·6	Os = 199	
H = 1			Cu = 63·4	Ag = 108	Hg = 200	
	Be = 9·4	Mg = 24	Zn = 65·2	Cd = 112		
	B = 11	Al = 27·4	? = 68	U = 116	Au = 197 ?	
	C = 12	Si = 28	? = 70	Sn = 118		
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210 ?	
	O = 16	S = 32	Se = 79·4	Te = 128 ?		
	F = 19	Cl = 35·5	Br = 80	I = 127		
Li = 7	Na = 23	K = 39	Rb = 85·4	Cs = 133	Tl = 204	
		Ca = 40	Sr = 87·6	Ba = 137	Pb = 207	
		? = 45	Ce = 92			
		?Er = 56	La = 94			
		?Yt = 60	Di = 95			
		?In = 75·6	Th = 118			

1. The elements arranged according to the magnitude of atomic weight show a periodic * change of properties.

2. Chemically analogous elements have atomic weights either in agreement (Pt, Ir, Os), or increasing by equal amounts (K, Rb, Cs).

3. The arrangement, according to atomic weights, corresponds with the *valency* of the elements, and to a certain extent the difference in chemical behaviour, for example, Li, Be, B, C, N, O, F.

4. The elements most widely distributed in nature have small atomic weights, and all such elements are distinguished by their characteristic behaviour. They are thus *typical* elements, and the lightest element, hydrogen, is therefore rightly chosen as the typical unit of mass.

5. The magnitude of the atomic weight determines the properties of the element, whence in the study of compounds regard is to be paid not only to the number and properties of the elements and their mutual action, but to the atomic weights of the elements. Hence the compounds of S and Te, Cl and I, show, beside many analogies, yet striking differences.

* Here an error in the German translation does an injustice to the original, inasmuch as the Russian word for periodical is rendered "stufenweise" (gradual).

6. It allows the discovery of many *new* elements to be foreseen, for example, analogues of Si and Al with atomic weights between 65 and 75.

7. Some atomic weights will presumably experience a correction; for example, Te cannot have the atomic weight 128, but 123 to 126.

8. From the foregoing table, new analogies between elements become apparent. Thus U appears as an analogue of B and Al, which, as is well known, has long ago been established experimentally.

Previous students of the subject had been, for the most part, struck with the relations obviously subsisting between the members of the several natural families of elements, but had, with few exceptions, failed to perceive that there must be a *general* law binding the whole together. However, Mendeléeff, with that noble sentiment of justice which always animates the truly scientific mind, admits that the idea of a general law had already been foreshadowed by others, and he says (Faraday Lecture, 1889), "I now see clearly that Strecker, de Chancourtois, and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen."

It may be remarked that Strecker did little more than call attention to the sequence in the values of the atomic weights of certain elements, and states that "we must leave to the future the discovery of the *law* of the relations which appear in these figures" (Theorien u. Experimente zur Bestimmung der Atom Gewichte der Elemente, 1859). De Chancourtois, in his work entitled "Le Vis Tellurique" (1863), devised a geometric method of representing the atomic weights by coiling round a cylinder a helix with an angle of 45°, the cylinder being divided vertically into sixteen equal parts by lines drawn from the circular base. The points of intersection of the helix with these lines were supposed to represent the atomic weights of elements which differed from one another by 16 or by multiples of 16.

Mendeléeff's table of 1869 was subsequently in 1871 modified so as to assume the form with which we have all been so long familiar, and which is to be found in every modern text-book. Thus it may be claimed for Mendeléeff that he was actually the first, not only to formulate a general law connecting atomic weights with properties, but was the first to indicate its character, and, as himself (*Principles*, 1905, II, p. 28) has pointed out, he was the first "to foretell the *properties of undiscovered* elements, or

to alter the accepted atomic weights" in confidence of its validity. The time was, in fact, ripe for the enunciation of this general principle, and, the suggestion once given, the relations embodied in the law could not fail to attract other chemists. Accordingly, in December, 1869, Lothar Meyer, with such knowledge of Mendeléeff's scheme as could be derived from the imperfect German version of his paper of the previous March, proved himself a convinced exponent of the idea by contributing to Liebig's *Annalen* a paper containing a table, substantially identical with that of Mendeléeff, and his famous diagram of atomic volumes, which, more clearly even than the tabular scheme, illustrates the principle of periodicity.

The history of science shows many instances of the same kind. Great generalisations have often resulted from the gradual accumulation of facts which, after remaining for a time isolated or confused, have been found to admit of co-ordination into a comprehensive scheme, and, this once clearly formulated, many workers are found ready to assist in its development. The case is nearly parallel to the recognition of the operation of natural selection by Darwin and Wallace, or it might be compared to the discovery of oxygen by Priestley and Scheele and the utilisation of this knowledge by Lavoisier. In each case much preparatory work had been done, and a body of knowledge had been gradually accumulated which, when duly marshalled and surveyed by the eye of a master, could scarcely fail to reveal to him the underlying principle. The full consequences, however, would appear only to a few.

The law of periodicity was expressed by Mendeléeff in the following words: *

"The properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence on, or (expressing ourselves algebraically) form a periodic function of, the atomic weights of the elements." After a brief historical account of the discovery of the law by himself, Mendeléeff concludes by saying (*Principles*, p. 18): "I consider it well to observe that no law of nature, however general, has been established all at once; its recognition has always been preceded by many presentiments; the establishment of a law, however, does not take place when the first thought of it takes form, or even when its significance is recognised, but only when it has been confirmed by the results of experiment which the man of science must consider as the only proof of the correctness of his conjectures and opinions."

* *Principles*, 1905, Vol. II, p. 17.

I regard it as unnecessary, in the presence of the Fellows of the Chemical Society, to review with any detail the multitudinous applications of the scheme of the elements constructed on the basis of the periodic law. These are the commonplaces of modern theoretical chemistry. They are embodied in every text-book of any importance, and are related by every lecturer and teacher as familiar and indisputably recognised consequences of the system. We may therefore pass lightly over the story of the prediction by Mendeléeff of the properties of undiscovered elements, confirmed so remarkably by the discovery of scandium, gallium, and germanium, and related in dramatic language by Mendeléeff himself (Faraday Lecture). We may also pass over the applications of the system to the correction of atomic weights, illustrated by the case of beryllium, the recognition of previously unnoticed relations, and the discovery of new elements, notably the companions of argon (Ramsay, Presidential Address to Section B, British Association, 1897, and *Proc. Roy. Soc.*, 1898, **63**, 437).

It will be more profitable to consider a few of the difficulties which still encumber the application of the law, and which, while limiting our acceptance of it in an unqualified form as applicable to the whole of the elements, tempt the speculative mind to wander in wide fields of conjecture.

Can it be truly said that the elements arranged in the order of their atomic weights show without exception periodic changes of properties? This question has been propounded already, but has never been fully discussed, even by Mendeléeff. An examination of the facts seems, however, to indicate the possibility of some other principle, which, while it does not supersede the periodic scheme, would, if it could be recognised, supplement it. This involves other considerations which we may turn to first.

If the whole of the known elements are drawn up in the order of their atomic weights (using the values given by the International Committee for 1908), we find a progression in value from H = 1·008 to U = 238·5, with differences between the successive elements which vary from 0·3 (Co − Ni) * to 4·3 (Co − Cu) among the

* Mendeléeff held the view that "in general, cobalt is more nearly allied to iron than nickel, and the latter more nearly to copper" (*Principles*, Eng. Ed., 1905, p. 379). Accordingly, in the first edition of his book, he assigned to cobalt the atomic weight 58·5, and to nickel, the atomic weight 59. In the later edition of 1905, he makes them both 59, and expresses the belief that eventually the atomic weight of cobalt will be found less than that now accepted and less than nickel (Eng. Ed., 1905, II, footnote 25, p. 45). Whatever may be the exact values of the atomic weights of these two elements, there can be no doubt that the atomic weight of cobalt is *greater* than that of nickel. This is proved by the estimations of the specific heats of both these metals purified by methods which preclude the possibility

common elements of which the atomic weights have been most accurately estimated. The large difference, 7·4, between Sb and Te is manifestly due to some error in the atomic weight of tellurium of which no sufficient explanation is yet forthcoming, and it is only when we get to the element Bi that there seems reason for thinking that it must be followed by some hitherto unrecognised elements, since the gap between Bi and the next known element, Ra, is 18·7 units. The atomic weights of the long series of elements beginning with La are confessedly uncertain, but that they all lie between La and Ta seems probable, because although the individual numbers are doubtless inexact, the *average* difference between any two consecutive terms is roughly the same as the average difference between successive atomic weights among the better known elements preceding them. $Ta - La = 181 - 138{\cdot}9 = 42{\cdot}1$ for sixteen intervals.

It must also be noted that the differences, approximately three units each, among the three elements with smallest known atomic weights, namely,

H 1·008, He 4, Li 7·03,

are greater than the differences observed among the elements which immediately succeed them, namely,

Li 7·03, Be 9·1, B 11, C 12, N 14·01, O 16, F 19.

It will be seen later that, as regards this part of the scheme, Mendeléeff had put forth a special hypothesis.

If these considerations are to be regarded as having weight, it seems probable that few additional elements are to be expected, except possibly one following Mo and another following W, save in the region already indicated from Bi to Ra. This suggests the remark that, after all, it is not necessary to assume that the materials of which the earth consists should necessarily include a sample of every possible element indicated by such a scheme. Some which are missing from terrestrial matters may perhaps be responsible for phenomena recognisable by the spectroscope in stars or nebulæ far distant in cosmical space. The unexpected, however, often happens, and, remembering the discovery of terrestrial

of appreciable error or of mutual contamination. The following results were obtained by different observers using different methods:

Temperature.	Cobalt.	Nickel.
From 100° to 15°	0·10303	0·10842
,, 15° to −78·4°	0·0939	0·0975
,, 78·4° to −182·5°	0·0712	0·0719

Tilden, *Phil. Trans.*, 1900, **194** *A*, 249.

From 100° to 20°	0·104	0·108

Copaux, *Compt. rend.*, 1905, **140**, 657.

helium, it is permissible to hope that some of the vacant spaces may hereafter be filled by earthly occupants.

There is one important point to be noted here, namely, that if the so-called rare earth metals, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, erbium, ytterbium, and others of which the existence is doubtful, do lie in the position indicated, the original statement of the periodic law breaks down at this point. Enough is already known of their properties to show that they are very closely allied together, and cannot fall into separate periods. Mendeléeff says (*Principles*, 1905, Vol. II, p. 45), "This appears to me to be one of the most difficult problems offered to the periodic law." He prefers, however, to leave open the question as to the position of these elements. The discordance of argon and of tellurium with the places assigned to them are also matters which must be left for the consideration of future workers.

One result of the recognition of the periodic law is that theories concerning the genesis of the elements have received a stimulus previously unknown. It is, however, interesting to note the attitude of Mendeléeff toward this question, and the small extent to which this attitude appears to have become modified with the lapse of time. When, in 1889, twenty years after the discovery of the law, he composed the Faraday lecture, he seems to have regarded speculation in this direction as a kind of abuse of the periodic system. He was, of course, fully justified in stating (Faraday Lecture) that "the periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connexion with that relic of the torments of classical thought." But it is at least questionable how far he was justified in continuing that "therefore it affords no more indication of the unity of matter, or of the compound character of our elements, than the law of Avogadro or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of a unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity, when it was found convenient to admit the existence of many gods and a unique matter." And again, later, "From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias."

Fifteen years later, after the discovery of the argon group of elements, of the phenomena of radioactivity, and of radium, it became necessary to consider the relations of these substances to the periodic scheme. In a remarkable article contributed to the new Russian Encyclopædia, and subsequently printed as Appendix III to the *Principles* (English Edition, 1905), Mendeléeff gives a new table of the elements, in which places are found, not only for the argon group and radium, but for two hypothetical elements which are placed before helium and designated x and y.

As this table may be assumed to represent his latest views concerning the relations of the elements, it is here reproduced.*

The y in the table is supposed to be an analogue of helium, and may be identified hereafter with "coronium," which has been recognised in the sun's coronal atmosphere. This gas would have, according to Mendeléeff, a density about 0·2, and therefore a molecular weight about 0·4, or about one-tenth that of helium.

x is the "ether" of the physicist, for which Mendeléeff, disregarding conventional views, supposes a molecular structure. He also assumes that, like the argon group, this element is chemically inert and possesses a very low density and atomic weight, estimated at 0·000,000,000,053.

His views in connexion with this matter are put forward merely as speculations and without dogmatism, but it is clear that he retained his repugnance to the conception of a unique matter to the last. In his essay entitled "A Chemical Conception of the Ether" (translated by Kamensky, 1904), the following passage occurs, p. 32: "Being unable to conceive the formation of the known elements from hydrogen, I can neither regard them as being formed from the element x, although it is the lightest of all the elements. I cannot admit this, not only because no fact points to the possibility of the transformation of one element into another, but chiefly because I do not see that such an admission would in any way facilitate or simplify our understanding of the substances and phenomena of nature."

Chemists and physicists have, however, found it impossible to resist the fascination of this problem, and accordingly there have been many hypotheses as to the origin of the elements and the nature of their connexion with one another. These seem to be inseparable from the periodic scheme itself, which at once provokes the inquiry, Why do these numerical relations occur, and what

* The spaces left vacant in Series I, after hydrogen, are the positions of hypothetical elements having approximately the atomic weights, 1·4, 1·8, 2·2, 2·6, 2·8, 3·0, and 3·4, and standing at the head of groups II to VIII respectively.

Series.	Zero group.	Group I	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.		
0 ...	x	—	—	—	—	—	—	—	—	—	—
1 ...	y	Hydrogen, H=1·008	—	—	—	—	—	—	—	—	—
2 ...	Helium, He=4·0	Lithium, Li=7·03	Beryllium, Be=9·1	Boron, B=11·0	Carbon, C=12·0	Nitrogen, N=14·04	Oxygen, O=16·0	Fluorine, F=19·0	—	—	—
3 ...	Neon, Ne=19·9	Sodium, Na=23·05	Magnesium, Mg=24·1	Aluminium, Al=27·0	Silicon, Si=28·4	Phosphorus, P=31·0	Sulphur, S=32·06	Chlorine, Cl=35·45	—	—	—
4 ...	Argon, Ar=38	Potassium, K=39·1	Calcium, Ca=40·1	Scandium, Sc=44·1	Titanium, Ti=48·1	Vanadium, V=51·4	Chromium, Cr=52·1	Manganese, Mn=55·0	Iron, Fe=55·9	Cobalt, Co=59	Nickel, Ni=59 (Cu)
5 ...	—	Copper, Cu=63·6	Zinc, Zn=65·4	Gallium, Ga=70·0	Germanium, Ge=72·3	Arsenic, As=75·0	Selenium, Se=79·0	Bromine, Br=79·95	—	—	—
6 ...	Krypton, Kr=81·8	Rubidium, Rb=85·4	Strontium, Sr=87·6	Yttrium, Y=89·0	Zirconium, Zr=90·6	Niobium, Nb=94·0	Molybdenum, Mo=96·0	—	Ruthenium, Ru=101·7	Rhodium, Rh=103·0	Palladium, Pd=106·5 (Ag)
7 ...	—	Silver, Ag=107·9	Cadmium, Cd=112·4	Indium, In=114·0	Tin, Sn=119·0	Antimony, Sb=120·0	Tellurium, Te=127	Iodine, I=127	—	—	—
8 ...	Xenon, Xe=128	Cæsium, Cs=132·9	Barium, Ba=137·4	Lanthanum, La=139	Cerium, Ce=140	—	—	—	—	—	—
9 ...	—	—	—	—	—	—	—	—	—	—	—
10 ...	—	—	—	Ytterbium, Yb=173	—	Tantalum, Ta=183·0	Tungsten, W=184	—	Osmium, Os=191	Iridium, Ir=193	Platinum, Pt=194·9 (Au)
11 ...	—	Gold, Au=197·2	Mercury, Hg=200·0	Thallium, Tl=204·1	Lead, Pb=206·9	Bismuth, Bi=208	—	—	—	—	—
12 ...	—	—	Radium, Rd=224	—	Thorium, Th=232	—	Uranium, U=239	—	—	—	—

is the meaning of them if they do not point to a common genesis or the operation of some process of evolution?

Hypotheses concerning the evolution of the elements have hitherto been usually based on the assumption that the successive stages of condensation of elemental matter proceeded from a single primary stuff, which by a process analogous to polymerisation among carbon compounds gave rise to atoms of greater and greater mass, which were stable at the prevailing and any lower temperature. The physical cause of the successive condensations is supposed to be a falling temperature. It is, of course, possible to imagine that if to the stuff of which hydrogen atoms consist are added successive portions of matter of the same kind, stable structures may at intervals result which we know as the atoms of the elements helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine, provided the idea of internal structure in these atoms is allowed. Otherwise, from the mere accretion of matter upon a central nucleus, there seems no sufficient reason why there should not have been formed an indefinite number of intermediate masses corresponding to an indefinite number of what would be called elements. Further, it is difficult to understand why simple increase of mass should change, say, oxygen into fluorine, while a further addition of the same kind should change negative fluorine into inert neon or positive sodium. The possibility of the condensation of a single "protyl" so as to produce, at successive though unequal stages of cooling, the elements known to the chemist has been most ably discussed long ago by Sir William Crookes.

This hypothesis, however, was put forward long before the work of Sir J. J. Thomson and his school was given to the world and the electron was accepted as a physical reality. The hypothesis that one elemental stuff may give rise to the whole array of known elements by a process of condensation accompanied by a loss or gain of electrons, the mass of which is approximately one-thousandth of the mass of an atom of hydrogen, forms the subject of a paper by Mr. A. C. G. Egerton in a recent number of our Transactions (1909, **95**, 239). The atomic weights calculated by his formula agree closely with the experimental atomic weights of the first fifteen elements, but the hypothesis gives no explanation of the facts observed in the physical properties of the elements arranged according to the Mendeléeff scheme, their alternation of odd and even valency, the transition from positive on one side of the table to negative on the other, the periodicity of properties shown by the sudden change of character in passing from fluorine to the next element, whether it be neon or sodium.

Another paper by Messrs. A. C. and A. E. Jessup (*Phil. Mag.*,

1908, [vi], **15**, 21) has recently provided a hypothesis of an entirely different character. From a study of the spectra of the nebulæ, these authors have been led to assume the existence of two hitherto unrecognised elements, to which the names protoglucinum and protoboron are assigned. These with hydrogen and helium are supposed to represent *four* initial substances, or protons, which, by condensation directly or indirectly, give rise to all the rest of the elements. The arguments of these authors are ingenious, but rather artificial in view of the fact that the number of groups in the periodic scheme to be provided for is greater than four.

In the Mendeléeff chart of the elements, there is nothing more striking than the gathering of the negative elements toward what may be called the N.E., and the segregation of the positive elements toward the S.W., the centre of the intermediate territory being occupied by elements which play a more or less undecided part. I have elsewhere (Presidential Address, 1905, Trans., **87**, 564) drawn attention to the fact that carbon, at any rate, is not directly deposited by electrolysis from any of its compounds, with positive hydrogen on the one hand, or negative chlorine on the other. I believe the same is true of silicon, these two elements standing in a middle position between the extremes occupied by lithium and fluorine respectively.

If we assume that atoms are made up of two parts (protyls), positive and negative, in proportions which determine by the preponderance of one or the other whether the element shall exhibit the positive character of a metal like lithium or the negative character of a halogen, we arrive at a hypothesis which recalls the ideas put forward nearly a century ago by Berzelius. His views are familiar to every student of the history of chemistry, but have long been relegated to the lumber room of worn-out doctrine. The last few years have, however, given us the remarkable experimental investigations of J. J. Thomson already referred to, and the new conceptions concerning the nature of atoms, which revive the fundamental idea that they are made up of two components.*

Carnelley, in 1885 (*Brit. Assoc. Reports*), brought forward the idea "that the elements are not elements in the strict sense of the term, but are, in fact, compound radicals made up of at least two simple elements, A and B." The element A was supposed to be identical with carbon, while to B was assigned a negative weight, −2, and it was suggested that it might be the ether of space. C. S. Palmer (*Proc. Colorado Scient. Soc.*) assumed the existence of two sub-elements, to which he gave the names "kalidium" and "oxidium," and his views appear to have a general resemblance to the hypothesis suggested in the text. The original article is abstracted in Venables' *Periodic Law* and is referred to in footnotes in Palmer's translation of Nernst's *Theoretical Chemistry*.

Setting out the known elements in the order of the numerical value of their atomic weights, we find that between the first three elements, H=1, He=4, and Li=7, the difference, 3, is greater than would be expected by comparison with the differences noticed between the elements of greater atomic weight which immediately follow them. In order to satisfy the hypothesis just put forward, there appears to be wanting an element which should stand in the same relation to fluorine as hydrogen to lithium. This would have an atomic weight 2·7 approximately. Whether this exists, and whether its existence is indicated by the unappropriated spectral lines of nebulæ or corona, can only be a matter of conjecture. Mendeléeff, in his (1905) latest speculations concerning the possibility of still undiscovered elements, has suggested the existence of a new element of the halogen group with an atomic weight about 3.* But, as already sufficiently shown, he accepted no hypothesis which involved any idea of the composite nature of the elements. It would therefore have been foreign to his system to employ this element in any such manner. But the idea seems to me to assist materially conceptions as to the process of condensation hypothetically occurring in the evolution of the known chemical elements. For to suppose that the typical elements, so different as they are in character, forming the first line of Mendeléeff's scheme, have all resulted from the condensation of a single protyl has always seemed to me a difficult proposition. There is comparatively little difficulty in the view that the successive terms of a family of what, by analogy, may be called a homologous series, may have originated in this way. A consideration of all the properties of the alkali metals, for example, coupled with the character of their spectra, suggests quite naturally the passage from lithium to sodium, and so forth, step by step, by the addition of successive accretions of the same matter to the primal element, the character of which, including valency, is not only sustained through the whole family, but becomes more strongly marked in proportion to the gradual increase of atomic weight. At the opposite end of the table, on the other hand, a *reduction* of the negative character of the element, in passing from fluorine to iodine, seems to suggest that the negative protyl which preponderates in the smaller atom is modified in the larger atom by the addition of a certain proportion of the positive protyl.

The conceptions presented to us in J. J. Thomson's work permit of several supplementary hypotheses, especially the idea that if

* It may also, perhaps, be worthy of note that Mr. Egerton's calculations (*loc. cit.*) lead him to postulate an element of nearly this atomic weight, namely, 2·9844, although his paper gives no indication as to its character.

atoms are really made up of smaller corpuscles these are not thrown together in confusion but, as he has shown, must be distributed within the mass in a definite order, which is determined by the attraction of the electro-positive shell and the self-repulsion of the negative corpuscles included in it. Once the idea of structure within the atom is admitted, the possibility presents itself of there being for the same mass more than one arrangement corresponding to what is called isomerism in compounds. In this way the case of elements with similar properties and identical or nearly identical atomic weights, for example, cobalt and nickel, and even such a case as tellurium, might perhaps be explained. Further, now that the materials which have so long received the unsatisfactory designation of the "rare earths" are found in unexpected abundance, it may be hoped that the study of their chemical characters may be completed. It may turn out that this group may include elements of identical atomic weight, though exhibiting different properties. It does not seem very long ago in the memory of many now living that the nature of the isomerism of the derivatives of benzene was a deep mystery, from which nearly all obscurity cleared away in the light of the then new theory of the constitution of benzene.

I have dwelt at some length on these various hypotheses, because the discussion of the subject to which they relate indicates, in my opinion, one of the consequences of the promulgation and general acceptance of the periodic scheme of the elements. This is, however, not the only result of the recognition of its validity and usefulness by chemists generally. That the elements stand in a definite relation to one another implies that their compounds also fall into their places in an orderly system, and consequently a basis is provided for the complete systematisation of the whole science of chemistry. There is scarcely a treatise on chemistry which does not bear evident witness to this influence. And this is perhaps not the least among the services rendered by this generalisation, for not only is the learner enabled to remember a much larger number of facts than previously, but he is led to perceive a connexion between phenomena and processes which was almost entirely wanting so long as practical chemistry consisted mainly of a bundle of recipes. And here it is fitting that we should glance at the famous treatise by Mendeléeff himself, "The Principles of Chemistry," of which we possess three editions in English, the last of which, issued in 1905, is a rendering of the seventh edition (1903) of the original. An eighth Russian edition began to be issued in 1905, but is incomplete. To this remarkable book it is impossible to do justice in a brief notice or to communicate to

those who have not read it an adequate impression. Clearly it is a work of genius, but such works are not always the most suitable for beginners, though for the advanced student nothing can be more inspiring. The "Principles" embody in reality two distinct treatises, for the text, which is written in an easy style, open to quite straightforward reading, is accompanied by notes which are often more voluminous and usurp entire pages. Even the preface is attended by these commentaries, which are all interesting as showing the spirit of the writer and the restless activity of his mind. A few extracts from the preface will serve to illustrate the truism too often neglected by writers of biographies, that it is impossible to separate a man's work from his life, and that the character and quality of the former are dependent upon the personal characteristics of the man, independently of the opportunities or influences which may have served to assist or to repress his activities.

"If statements of fact," he says, "themselves depend upon the persons who observe them, how much more distinct is the reflection of the personality of him who gives an account of methods and philosophical speculations forming the essence of a science! For this reason there will inevitably be much that is subjective—bearing the stamp of time and locality—in every objective exposition of science. And as an individual production is only significant in virtue of that which has preceded it and that which is contemporary with it, it resembles a mirror, which in reflecting exaggerates the size and clearness of neighbouring objects, and causes a person near it to see reflected most plainly those objects which are on the side to which it is directed, and sometimes even the person holding the mirror. Although I have endeavoured to make my book a true mirror directed toward the whole domain of chemical changes and of the elements taking part in them, yet involuntarily those influences near to me being most clearly reflected and the most brightly illuminated have tinted the entire work with their colouring. In this way the chief peculiarity of the book has been determined. Experimental and practical data and their application in life and industry occupy their place, but the philosophical principles of our science form the chief theme of the work."

Later on he says, "The thought that this book might fall not only into the hands of the beginner for whom it is intended, but also of authorities who might wish to know the views held by an old disciple of science on the current problems of chemistry, greatly complicated the preparation of a new edition, for it necessitated making a selection of the most essential of the vast number of

new researches published year by year and explaining my views on them without greatly enlarging the bulk of the work. After having closely followed all the chief conquests of chemical science since the days of Berzelius, Liebig, Dumas, and Gerhardt, and having seen the triumph of much that lay neglected, and the fall of much that was exalted, I involuntarily acquired a tendency to analyse new facts, and a desire to transmit to my readers the results of such analysis, if it could, in my opinion, help towards a proper explanation and generalisation of the chemical elements. In carefully preparing this edition, I have not lost sight of the fact that I am hardly likely to publish another, and I have therefore in many cases spoken more definitely than formerly. After having been an insignificant but zealous worker in chemistry for almost half a century, I wished my book should retain some traces of how a confirmed disciple of Gerhardt regards the fundamental problems of the theory of the chemical elements at the beginning of the twentieth century. As an example, I may mention that the more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter, and from the hope of attaining the desired end by a study of electrical and optical phenomena, and the more clearly have I recognised that first and foremost are needed truer conceptions of 'mass' and 'ether' than those in vogue at the present time. The return to electrochemism which is so evident in the supporters of the hypothesis of 'electrolytic dissociation,' and the notion of a splitting up of atoms into 'electrons,' in my opinion only complicate, and in no way explain, so real a matter (since the days of Lavoisier) as the chemical changes of substances, which led to the recognition of the invariable and ponderable atoms of simple bodies. The definition of mass gave a means for analysing and grasping chemical transformation of substances, and for arriving at the atom, while the mass of the atom was shown by the periodic law to influence all its chief chemical properties. Thus chemistry in its principles stood on the firm foundations laid by Galileo, Newton, and Lavoisier, and in order to gain further insight and knowledge of the atoms themselves, the fundamental conceptions of mass, gravity, and ether will have to be explained by a method of experiment alone, otherwise the realism of science will again open its doors to such metaphysical and 'metachemical' conceptions as phlogiston and other mystical dreams. For my part I endeavour to remain true to the testament of realism left by Newton and Lavoisier, and it is my wish to instil this sentiment into my young readers."

This is very clear, and little more remains to be said. In the seventeenth century Robert Boyle taught us how to distinguish elements from compounds, and how to give to the word "element" a definite connotation clearly distinguishing it from the elusive and fantastic language of the alchemists. In the eighteenth century Lavoisier showed the true nature of the most familiar of chemical compounds, namely, acids, bases, and salts, and helped to lay the foundation of quantitative chemistry. At the beginning of the nineteenth century Dalton gave to chemistry the Atomic Theory, of which it is not too much to say that it provided the scaffold by the aid of which the entire fabric of modern theoretical chemistry has been built up. Sixty years later this conception, developed and adorned by the labours of an army of earnest workers, has been shown to us in a brilliant new light thrown over the whole theory by Mendeléeff.

The views of Boyle, of Lavoisier, and of Dalton have been corrected by experience and broadened by extended knowledge, but the fundamental and essential parts of their ideas remain, and their names are immortal. In like manner the expression of the periodic law of the elements as known to the present generation is destined, we may believe, to be absorbed into a more comprehensive scheme by which obscurities and anomalies will be cleared away, the true relations of all the elements to one another revealed, and doubts as to the doctrine of evolution resolved in one sense or the other. But as with the Atomic Theory itself, there is no reason to doubt that the essential features of the periodic scheme will be clearly distinguished through all time, and in association with it the name of Mendeléeff will be for ever preserved among the Fathers or Founders of Chemistry.

THOMSEN MEMORIAL LECTURE.

Delivered on February 17th, 1910.

By Sir Edward Thorpe, C.B., LL.D., F.R.S., Past-President of the Chemical Society.

Among the Danes whose names are inscribed as men of science on the eternal bead-roll of fame, that of Julius Thomsen stands pre-eminent—linked indeed with that of Oersted. It is significant of the position which Thomsen acquired in physical science, and of the respect which that position secured for him in the eyes of his countrymen, that his statue should have been erected during his lifetime and placed in the vicinity of that of Oersted in the court-yard of the Polytechnic High School of Copenhagen. Thomsen, in fact, played many parts in the intellectual, industrial, and social development of Denmark. To Europe in general he was mainly known as a distinguished man of science. By his fellow-citizens he was further recognised as an educationist of high ideals, actuated by a strong common sense and a stern devotion to duty; as an able and sagacious administrator; as a successful technologist and the creator of an important and lucrative industry based upon his own discoveries; and as a man of forceful character, who brought his authority, skill, and knowledge of men and affairs to the service of the communal life of Copenhagen.

Thomsen was a municipal councillor of that city for more than a third of a century. He occupied a commanding position on the Council, and was invariably listened to with respect. The gas, water, and sewage works of Copenhagen are among the monuments to his civic activity. From 1882 up to the time of his death he was a member of the Harbour Board of the port. In these respects Thomsen sought to realise Priestley's ideal of the perfect man—that he should be a good citizen first and a man of science afterwards.

Hans Peter Jürgen Julius Thomsen was born in Copenhagen on February 16th, 1826. He was educated at the church school of St. Peter in that city, and subsequently at von Westens Institute. In 1843 he commenced his studies at the Polytechnic, and in 1846 graduated there in Applied Science, and became an assistant to Professor E. A. Scharling. Of his earliest years comparatively little is known. Thomsen, always a reserved and taciturn man, talked little about himself even to his intimate friends—and least of all about the days of his youth. It was known to a few that these days had not been smooth. Those who were best informed

were conscious that to these early struggles much of that dour and resolute nature which formed a distinguishing trait in his character was due. Thomsen, indeed, began life as a fighter, and a fighter he remained to the end of his four-score years.

In 1847, he became assistant to Forchhammer, passing rich, like Goldsmith's pedagogue, on £40 a year. Georg Forchhammer, whose earliest work dates back to the period when Berzelius was in his prime, was an active and industrious investigator of the old school, mainly in inorganic chemistry, and more particularly on problems of chemical geology and physiography. He was a frequent visitor to this country, and was well known to early members of the British Association. Although doubtless influenced, in common with all teachers in Northern Europe, by the example and methods of Berzelius, such influence as he himself was able to exert died with him. Forchhammer attracted few pupils, and created no school, and Thomsen probably derived no inspiration or acquired any stimulus from this association. For a time Thomsen supplemented his scanty income by teaching agricultural chemistry at the Polytechnic. In 1853 he obtained a travelling scholarship, and spent a year in visiting German and French laboratories. He probably owed this scholarship in great measure to his first contribution to the literature of chemistry, namely, his memoir, "Bidrag til en Thermochemisk System" (contributions to a thermochemical system), communicated to the Royal Society of Sciences of Copenhagen in 1852, and for which he received the silver medal of the Society and a sum of ten guineas to enable him to procure a more accurate apparatus. In this memoir he sought to develop the chemical side of the mechanical theory of heat, doubtless under the influence of Ludwig Augustus Colding, an engineer in the service of the Municipality of Copenhagen, and a pioneer, like Mayer, in the development of that theory. Indeed, the Danes now claim for Colding, who had made experiments on the relation between work and heat as far back as 1842, but whose labours were practically ignored by his contemporaries, the position which the Germans assign to Mayer (see Mach's "Development of the Theory of Heat"). In 1861 Thomsen further developed his ideas in a memoir on the "General Nature of Chemical Processes, and on a Theory of Affinity Based Thereon," published in the Transactions of the Danish Academy of Sciences. In this paper he laid the foundations of the chief scientific work of his life.

In 1853 Thomsen patented a method of obtaining soda from cryolite, so-called "Greenland," or ice-spar, a naturally occurring fluoride of sodium and aluminium, $Al_2F_6,6NaF$, found largely, indeed, almost exclusively, in Greenland, and particularly at

Ivigtut. It derives its mineralogical name from its ice-like appearance and ready fusibility even in the flame of a candle. It seems to have been first brought to Europe in 1794, and to have been described by Schumacher in the following year. Klaproth first showed that it contained soda, and its composition was further established by Vauquelin, Berzelius, and Deville.

Thomsen's process consists in heating a finely divided mixture of cryolite and chalk in a reverberatory furnace, whereby carbon dioxide is expelled and calcium fluoride and sodium aluminate are formed. The roasted mass is lixiviated with water, so as to dissolve out the sodium aluminate, which is then treated with carbon dioxide. Alumina is precipitated, and sodium carbonate remains in solution. The alumina is either sold as such, or converted into sulphate (so-called "concentrated alum" or "alum-cake"), and the sodium carbonate is separated by crystallisation. Both products are obtained in a remarkably pure condition, and the cryolite-soda yields excellent "caustic."

Thomsen's process, although simple enough in principle, requires considerable skill and pains in its practical execution, and most of the manufacturing details were worked out by him, or under his direction. Success largely depends upon the maintenance of a proper temperature; the decomposition begins below a red-heat, but requires to be finished at that temperature, and care must be taken to avoid fusion or even sintering of the mass. In 1854 Thomsen obtained the exclusive right of mining for cryolite and of working up the mineral in Denmark for soda and alumina. Actual manufacturing operations were begun on a small scale in 1857, and in the following year Thomsen planned the present large factory at Oeresund, near Copenhagen, which was opened on his thirty-fourth birthday. The importance of this industry to Denmark may be seen from the circumstance that during the fifty years of its existence the firm have paid the Danish Government nearly £300,000 for the concession. Other factories were started in Germany, Bohemia, and Poland, but met with little success. The Pennsylvania Salt-manufacturing Company at Natrona, near Pittsburg, eventually obtained the right to work up two-thirds of all the cryolite mined in Greenland. From the start Thomsen took a large share in the management of the Oeresund works, and by his energy, foresight, and skill placed the undertaking on a sound commercial basis.

Although Thomsen died a rich man, mainly as the result of the industry he created, in the outset of his career as a teacher and a technologist his means were very straitened. He came of poor parents, of no social position or influence, and they were unable to

further his inclinations towards an academical career. In 1854 he applied unsuccessfully for a position as teacher of chemistry at the Military High School in Copenhagen. During three years—from 1856 to 1859—while still engaged in developing his cryolite process, he acted as an adjuster of weights and measures to the Municipality of Copenhagen. It was a poorly paid position, but it kept the wolf from the door. At about this period he betook himself to literature, and published a popular book on general subjects connected with physics and chemistry—somewhat in the style of Helmholtz's well-known work—entitled "Travels in Scientific Regions," which had a considerable measure of success. He was, however, not altogether unknown even at this time as an author, since in 1853 he had collaborated with his friend Colding in producing a memoir on the causes of the spread of cholera and on the methods of prevention, which attracted much attention at the time of its appearance.

In 1859, whilst engaged in the Oeresund factory, he again applied to the authorities for a position as teacher at the Military High School, and succeeded in obtaining an appointment to a lectureship in physics, which he held until 1866. During his tenure of this office he devised his polarisation battery, which received many awards at International Exhibitions and was used for a time in the Danish telegraph service.

In 1859-60 he was "vicarius" for Scharling at the University, and in 1865 became a teacher, and in the following year Professor of Chemistry and Director of the Chemical Laboratory, a position which he retained—active to the last—until 1901, when he retired in his seventy-fifth year of age.

Before his connexion with the University, he founded and edited, from 1862 to 1878, in association with his brother, August Thomsen, the *Journal of Chemistry and Physics*, one of the principal organs of scientific literature in Denmark.

In 1863 he was elected a member of the Commission of Weights and Measures, and was instrumental in bringing about the adoption of the metric system and the assimilation of the Danish system to that of the Scandinavian Kingdom.

In 1883 Thomsen became Chancellor of the Polytechnic High School of Copenhagen—a position which he held for about nine years. During this period he entirely changed the character and spirit of the school, and stamped it with the impress of his earnestness and industry. Under his direction, new buildings were erected and arranged in accordance with the best Continental and American models. Thomsen's administration was in marked contrast to that of his somewhat easy-going predecessor, but it is doubtful if it

brought him popularity in the school. The students respected and even feared him, but his cold and unsympathetic nature evoked no warmer feeling. It was said of him by one who knew him intimately that he never learned to draw the young to him, to create in them an interest for his work, to form a school. Thomsen was a homely man, but not even in his home, says the same authority, was it possible for him to change his active, earnest, strenuous disposition—what his friends called his fighting character. But if he was always the serious master of the house, he was also its obedient servant. In reality he was a man of deep feeling, and was not without power to give that feeling expression in words, sometimes in verse, and occasionally even in music.

It was while occupying the position of Director of the Chemical Laboratory of the University that Thomsen executed the thermochemical investigations which constitute the experimental development of the ideas he had formulated in his memoir of 1861. The results of these inquiries were first made known in a series of papers published from 1869 to 1873 in the Transactions of the Royal Danish Society of Sciences, and from 1873 onwards by the *Journal für Praktische Chemie*. The papers were republished in collected form in four volumes (1882-1886) by a Leipzig house under the title of *Thermochemische Untersuchungen*. A summary of this experimental labour, which extended over a third of a century, was subsequently prepared by Thomsen, and published in 1905 in Danish under the title of *Thermokemiske Resultater*.

In this work he reviewed the whole of the numerical and theoretical results, to the exclusion of the greater portion of the experimental details. A translation of this volume by Miss Katharine A. Burke, entitled "Thermochemistry," renders it readily accessible to English readers. Miss Burke has supplemented the original work by a short account, taken from the *Thermochemische Untersuchungen*, of the experimental methods employed, thereby rendering the whole more intelligible to the student. Moreover, in the English edition a partial attempt has been made to translate Thomsen's deductions into the language of modern theory based on the conception of ionisation, which, of course, was not known to science at the time the *Thermochemische Untersuchungen* was published.

It is impossible within the limits of such a notice as this to deal in detail with the immense mass of experimental material which this work embodies, and I shall not attempt, therefore, to do more than to offer a generalised statement, based mainly upon the admirable account of Thomsen's work given by Professor Brönsted to the Chemical Society of Copenhagen on the occasion of the

meeting held on March 2nd, 1909, to commemorate Thomsen's services to science.

The conception of affinity as a cause and determining condition of chemical change is traceable in some of the earliest efforts to co-ordinate and explain chemical phenomena. It certainly existed long prior to the time of Boyle, and was at the basis of every philosophical system after his period. We need only mention the names of Bergman, Wenzel, and Berthollet to indicate this fact. But to Thomsen belongs the credit of being the first to make the attempt to measure the relative value or strength of affinity quantitatively, and to express it numerically in definite terms which admitted of exact comparison. Thomsen's theory of affinity, as enunciated by him in his 1851 paper, was based upon his conviction that affinity could be measured quantitatively by estimating the amount of heat evolved in the chemical process. We are not immediately concerned to show whether the theory is right or wrong, or in what respect it fails. The point is that the enunciation of this principle upwards of half a century ago constituted an important step forward, inasmuch as it sought to estimate affinity in relation to a quantity which can be fixed by experiment, and is capable of expression by numbers.

In this and in the subsequent paper of which mention has been made already, he thus defines his conception of thermochemistry, and discusses, for the first time, its laws.

"The force which unites the component parts of a chemical compound is called affinity. If a compound is split up, whether by the influence of electricity, heat, or light, or by the addition of another substance, this affinity must be overcome. A certain force is required the amount of which depends on the strength of the affinity.

"If we imagine, on the one side, a compound split up into its component parts, and on the other side these parts again united to form the original compound, then we have two opposite processes the beginning and end of which are alike. It is therefore evident that the amount of the force required to split up a certain compound must be the same as that which is evolved if the compound in question is again formed from its component parts.

"The amount of force evolved by the formation of a compound can be measured in absolute terms; it is equal to the amount of heat evolved by the formation of the compound.

"Every simple or complex action of a purely chemical nature is accompanied by evolution of heat.

"By considering the amount of heat evolved by the formation of a chemical compound as a measure of the affinity, as a measure

of the work required again to resolve the compound into its component parts, it must be possible to deduce general laws for the chemical processes, and to exchange the old theory of affinity, resting on an uncertain foundation, for a new one, resting on the sure foundation of numerical values."

As has been proved by later theoretical and experimental investigations, the theory of thermochemical affinity is not absolutely correct at ordinary temperatures. But, on the other hand, it has been shown that a comparatively large number of processes are approximately in unison with it. Not only do they agree qualitatively, that is to say, that heat is evolved during the process, but also in the fact that the results which newer and more exact methods for estimating affinity have produced, agree numerically with what would be required by the thermochemical theory. We meet here with a fundamental phenomenon which Thomsen deserves great credit for having first pointed out, but the explanation of which could not be given at the time he indicated it. It can be demonstrated theoretically that the lower we reduce the temperature and the nearer we get to the absolute zero, the more nearly is the condition for the theory fulfilled, so that at the absolute zero the theory would be found to be an exact law of nature. If it were possible to work at such low temperatures it would be found that the evolution of heat, or the evolution of energy by the chemical process, would be an exact measure of the affinity of the process, and that under this condition the theory of Thomsen would be the accurate expression of a natural law.

But under ordinary conditions this is not so, for in reality an ever-increasing number of endothermic processes are found to occur, that is, processes which proceed with the absorption of heat. Thomsen tried at first to explain these phenomena in such a way as to keep them within his system, and he drew a distinction between a purely chemical process running conformably to his theory and a physico-chemical process which did not fall within the law. But he was gradually convinced that his theory could not be maintained in its entirety. It is to his credit that he did not seek to uphold an untenable principle, or try to defend it as did Berthelot, who almost to his dying day maintained the validity of the principle in spite of all facts.

These ideas have, in the words of Ostwald, been the scientific confession of faith of chemists throughout half a century. They have had the greatest influence on scientific thought in every branch of chemistry. It is on the basis of them that we have arrived at a theory of affinity which at the present moment is being developed into one of the most perfect chemical theories.

Lastly, it is due to these ideas that the experimental material has been produced which during all time will place the name of Julius Thomsen in the first rank of men of science.

To go through this material in detail is, as I have said, impossible here. It may be stated generally that practically every simple inorganic process has been investigated calorimetrically by Thomsen, or can be calculated by means of the calorimetric data furnished by him. In the case of organic substances, data have been given for estimating the heat of combustion of a large number of compounds. All these estimations were made by Thomsen personally, according to a pre-arranged plan, and in systematic succession during a period of more than thirty years. They comprise more than 3500 calorimetrical estimations. It has been truly said that this work is unique in the chemical history of any country.

Among the results of Thomsen's thermochemical inquiries which have special value for physical chemistry is his investigation of the phenomena of neutralisation, in which he shows that the basicity of acids can be estimated thermochemically, and that it can in this way be proved whether or not a point of neutrality exists. His observation that the heat of neutralisation is the same for a long series of inorganic acids, such as hydrochloric acid, hydrobromic acid, hydriodic acid, chloric acid, nitric acid, etc., supports the theory of electrical dissociation, inasmuch as this requires that the heat of neutralisation of the strong acids must in all cases be independent of the nature of the acid, because the process of neutralisation for all of them is the combination of the ion of hydrogen in the acid with the ion of hydroxyl of the base to form water. These investigations also led to the important thermochemical result that the heat of neutralisation of acids (or the heat of their dissociation) cannot be considered as a measure of the strength of the acids.

Another important result is the proof by experiment of the connexion which exists between the changes of the heat-effect with the temperature and the specific heat of the reacting substances. The first law of thermodynamics requires the relation indicated by Kirchhoff: $\frac{dU}{dT} = C_1 - C_2$, where U is the heat-effect, T the temperature, and C_1 and C_2 are the heat capacities of the two systems before and after the reaction, and Thomsen showed by investigation of the heat of neutralisation, the heat of solution, and the heat of dilution, that this relation was satisfied For the purpose of his inquiry, the specific heats of a large number of solutions of salts were estimated by an ingenious method, and with an exactness hitherto unattained.

Of no less importance are Thomsen's thermochemical investigations on the influence of mass. In the year 1867 Guldberg and Waage published their theory of the chemical effect of mass. But they had only verified the theory to a small extent and in particularly simple cases. They had not investigated the complete homogeneous equilibrium, because at that time no method existed for experimental investigation of such homogeneous equilibrium. Thomsen showed that the estimation could be made thermochemically. By allowing, for instance, an acid to act on a salt of another acid in an aqueous solution, the latter acid will be partly replaced by the first, which will form a salt. By mixing, for instance, a solution of sodium sulphate and nitric acid, there is formed sodium nitrate and sulphuric acid, but the process will not proceed to completion. If we have estimated the heat of neutralisation of the two acids with sodium hydroxide, the difference between these two heat-phenomena will give the amount of heat corresponding to the total decomposition of the sodium sulphate, and the heat found experimentally by mixing the two solutions will therefore show to what degree the transformation has taken place. It would be possible to estimate thermochemically the amount of the four substances in solution, and thereby, by varying the concentration or the proportion between the initial quantities of substances, to calculate whether the Guldberg-Waage theory on the effect of mass was confirmed in this case.

Thomsen applied this method to a large number of different acids and bases, and was enabled thereby to prove the agreement with the law of the influence of mass in all the cases which he examined. He found particularly that the proportion of the one acid which remained combined with the base was constant with mixtures of constant proportion. On this basis he propounded the term *avidity*, which he defined as the tendency of the acid to unite with the base, and he showed that the avidity was independent of the concentration, and only to a small extent varied with the temperature. The term avidity has since acquired great importance, particularly since other and more exact methods for its estimation have been found. Concurrently with this, its meaning has been made clear by the theory of electrolytic dissociation.

On the basis of these estimations, Thomsen drew up the first table, based on experiments, of the relative strength of the acids, and the numbers in this table have been found to agree with the results obtained by examining the electrical conductivity of the acids.

It is worth noting that Thomsen not only produced the experimental proof of the correctness of the Guldberg-Waage theory of

the effect of mass soon after the appearance of this theory, but also that he was the first to acknowledge and adopt it. It is remarkable that this work of Thomsen received so little attention, although it appeared in a widely circulated German journal, and it was not until ten years later that the law of the effect of mass was generally recognised, as the result of the work of Ostwald and van't Hoff.

Although Thomsen's title to scientific fame rests mainly upon his thermochemical work, his interests extended beyond this particular department of physical chemistry. He worked on chloral hydrate, selenic acid, on ammoniacal platinum compounds, and on glucinum platinum chloride, on iodic acid and periodic acid, on hydrogen peroxide, hypophosphorous acid, and hydrogenium. He early recognised the importance of Mendeléeff's great generalisation, and contributed to the abundant literature it produced. His paper of 1895, "On the Probability of the Existence of a Group of Inactive Elements," may be said to have foreshadowed the discovery of the congeners of argon. He pointed out that in periodic functions the change from negative to positive value, or the reverse, can only take place by a passage through zero or through infinity; in the first case, the change is gradual, and in the second case it is sudden. The first case corresponds with the gradual change in electrical character with rising atomic weight in the separate series of the periodic system, and the second case corresponds with a passage from one series to the next. It therefore appears that the passage from one series to the next in the periodic system should take place through an element which is electrically indifferent. The valency of such an element would be zero, and therefore in this respect also it would represent a transitional stage in the passage from the univalent electronegative elements of the seventh to the univalent electropositive elements of the first group. This indicates the possible existence of a group of inactive elements with the atomic weights 4, 20, 36, 84, 132, the first five numbers corresponding fairly closely with the atomic weights respectively of helium, neon, argon, krypton, and xenon (*Zeitsch. anorg. Chem.*, 1895, **9**, 283; *Journ. Chem. Soc.*, 1896, **70**, II, 16). He subsequently made known the existence of helium in the red fluorite from Ivigtut.

As evidence of Thomsen's manipulative ability and his power of accurate work may be mentioned his determination of the atomic weights of oxygen and hydrogen, and incidentally of aluminium. For the atomic weight of hydrogen he obtained the value 1·00825 when O = 16, which is practically identical with that of Morley and Noyes. He further made most accurate estimations of the relative

densities of these gases, and of the volumetric ratios in which they enter into the composition of water. His value for the atomic weight of aluminium is nearly identical with that adopted in the last Report of the International Committee on Atomic Weights.

Thomsen maintained his interest in thermochemical problems up to the end, and was a keen and clear-sighted critic of the work which appeared from time to time during the later years of his life. This interest occasionally gave rise to controversy, and some of his latest papers were wholly polemical.

Thomsen was a pronounced atomist, and to him a chemical process was a change in the internal structure of a molecule, and the chief aim of chemistry was to investigate the laws which control the union of atoms and molecules during the chemical process. He considered that chemistry should be treated mathematically as a branch of rational mechanics. But no one insisted more strongly than he how little we really know of these questions. In summarising his theoretical ideas in the *Thermokemische Resultater*, he says, "An almost impenetrable darkness hides from us the inner structure of molecules and the true nature of atoms. We know only the relative number of atoms within the molecule, their mass, and the existence of certain groups of atoms or radicles in the molecule, but with regard to the forces acting within the molecules and causing their formation or destruction our knowledge is still exceedingly limited." He fully realised that his own work was only the foundation on which the future elucidation of these questions must rest. "He worked," says Brönsted, "in the conviction that what we somewhat vaguely call the affinity of the atoms—their interaction, their attraction, and varying effect, etc.—follows the general laws of mechanics, and that, as he worded it, the principle that 'might is right,' holds good in chemistry as in mechanics. On this foundation he hoped to be able to evolve the laws for the statics and dynamics of chemical phenomena, even although the true nature of the action is unknown."

Thomsen's merits as an investigator received formal recognition from nearly every country in the civilised world. As far back as 1860 he was elected one of the thirty-five members of the Danish Royal Society of Sciences of Copenhagen, and from 1888 until his death he was its President. In 1876 he became an Honorary Foreign Member of the Chemical Society of London. On the occasion of the fourth centenary of the foundation of the University of Upsala (created in 1477), he received the degree of Doctor of Philosophy *honoris causa*. In 1879 he was made an honorary M.D. of the University of Copenhagen. Two years later he was made a

Foreign Member of the Physiographical Society of Lund, and in 1888 he was elected a member of the Society of Science and Literature of Gothenburg. In 1885 he became a member of the Royal Society of Sciences of Upsala, and in 1886 of the Stockholm Academy of Sciences.

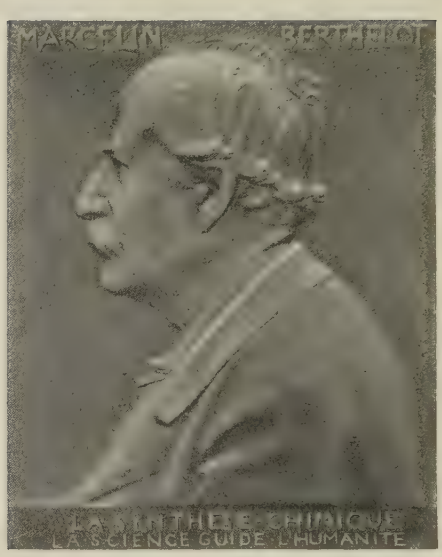
In 1883 he and Berthelot were together awarded the Davy Medal of the Royal Society—a fitting and impartial recognition on the part of the Society of the manner in which the two investigators, whose work not infrequently brought them into active opposition, had jointly and severally contributed to lay the foundations of thermochemistry.

In the same year Thomsen was made a member of the Accademia dei Lincei of Rome, and in the following year he was elected into the American Academy of Arts and Sciences in Boston, and of the Royal Academy of Sciences of Turin. In 1887 he was made a member of the Royal Belgian Academy.

In 1886-87 and again in 1891-92 he was Rector of the University of Copenhagen. In 1888 he became Commander of the Dannebrog, and in 1896, and on his seventieth birthday, he was made Grand Commander of the same order. On the same occasion the Danish chemists caused a gold medal to be struck in his honour. In 1902 he became a Privy Councillor (Geheime Konferenz raad). In the same year he was elected a Foreign Member of the Royal Society of London.

He died on February 13th, 1908, full of years as of honours, and was buried on the eighty-third anniversary of his birth and on the jubilee of the opening of the Oeresund factory. His wife, Elmine Hansen—the daughter of a farmer on Langeland—predeceased him in 1890.

I desire to express my acknowledgments to Director G. A. Hagemann, of Copenhagen, and to Professor Arrhenius, of Stockholm, for their assistance in obtaining information concerning Thomsen's personal history. I am also much indebted to our Fellow, Mr. Harald Faber, for his kindness in making for me a translation of Professor Brönsted's account of Thomsen's scientific work, on which my own résumé is mainly based.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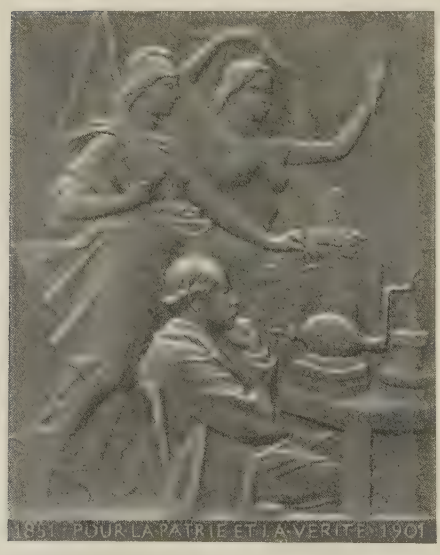
1851 POUR LA PATRIE ET LA VERITE 1901

BERTHELOT MEMORIAL LECTURE.

DELIVERED ON NOVEMBER 23RD, 1911.

By HAROLD BAILY DIXON, M.A., Ph.D., F.R.S., Past-President of the Chemical Society.

(1) *His Career.*

IN this age of extreme specialisation, the life and work of Berthelot teach the world the much-needed lesson that men of science are not necessarily men of one idea, but may be great, not only as experimenters, but great also as thinkers and as citizens. On *all* that he turned his mind to—and few things were foreign to his interest—Berthelot brought to bear, not only an exact scientific method and an exquisite clearness of statement, but an imagination as foreseeing as it was comprehensive, a patriotism as pure as it was enlightened. In the work of his life—whether as a philosopher or as a Cabinet Minister—Berthelot looked to Science as his guide. He believed in science as an illuminating and humanising force; he believed that in science lay the secret of the progress of France and of mankind. To pursue science was to ensure progress; science was to him a mission, a recreation, a religion. "To the end of my life," he wrote half-sadly to Renan (in 1892), "I shall be the dupe of this desire for progress which you so wisely relegate to the sphere of illusions." But of the reality of the progress achieved by Berthelot no chemist can doubt. In the realm of industry alone what tempting offers were made to him for a monopoly of his synthetic processes in organic chemistry. But Berthelot never bargained with or patented his discoveries. "The man of science," he declared, "should make the possession of Truth his only riches." Not that Berthelot considered the applications of science beneath him; on the contrary, he believed that science should be pursued largely by reason of its service to mankind. "Science has a double aim," he wrote, "an ideal aim which is the search for pure truth, and a positive and human aim which is the good of man and the development of civilisation."

Pierre Eugène Marcelin Berthelot* was born in the heart of the old Paris, in the Place de Grève—now Haussmannised out of recognition into the Place de l'Hôtel de Ville—on October 25th, 1827.

* I am indebted to the kindness of Berthelot's son—Prof. Daniel Berthelot—for exact names and dates, and also for much other valuable information. I desire also to express my obligation to my old student, Mr. A. S. Robinson, for making me a *précis* of Berthelot's papers.

He died in Paris, March 18th, 1907. As he was born and bred, so he lived and died a Parisian.

Through his father, Dr. Jacques Martin Berthelot, the son inherited his scrupulous regard for duty, his serious love for science, his liberal instincts, and his philosophic outlook on life; through his mother, Ernestine Sophie Claudine Béard, he inherited his ardent and responsive nature, his amazing industry, his versatility, and his curiosity. From the Place de Grève his family moved to a house near by in the narrow Rue des Ecrivains, just opposite the Tour Sainte-Jacques. The somewhat delicate and highly-strung boy grew up in sight of those royal ceremonials—the Corpus Christi processions from the Tuileries to Notre Dame—when people in the street were obliged to kneel, under penalty of sacrilege, as the procession passed. As a child the roar of the revolution must have sounded in his ears, for his father's house overlooked the scene of many of those deeds of violence that marked the popular upheaval against the Ordinances of the 25th of July (1830). Then, as again in the later revolutions, the house became a hospital equally for Royalist and for Republican, for Dr. Berthelot made no distinction between his patients, however much his sympathy went out to the suffering people.

Even from the age of ten, Berthelot tells us, he began to ponder on the problems of life, and was troubled by the insecurity of the future. Nevertheless, he was an industrious and brilliant scholar, and made rapid progress at the school he attended—the Collège Henri IV. Sixty years later at the Jubilee Celebration, M. Fouqué, the President of the Académie des Sciences, bore striking testimony to Berthelot's gifts as a boy. "Everyone admires in you your power of work, your spirit of invention, your logic of ideas, your grasp of memory, your skill in experiment. . . . I affirm that these precious gifts you already possessed in the germ when you were still a simple schoolboy. More than half a century ago we sat side by side on the benches of the mathematical class in the Collège Henri IV.; a close comradeship grew up between us. My recollections bring back with pleasure the long talks we had on every kind of question. . . . I still see myself in discussion with you on the muddy road that led to your house at the foot of the Tower of Saint-Jacques. There I met the kindest greeting from your father, and then we climbed to your attic and resumed our interrupted argument—our only distraction being the swallows that built among the sculptures of the old tower."

At the end of his school course in 1846 he took the highest prize in competition with all the best students from the lycées of Paris—

the "prix d'honneur de philosophie." To his sound classical education he attached great value, and his love of ancient literature lasted through life. Two old editions of Lucretius and of Tacitus, preserved from his schooldays, were his constant companions whenever he left Paris. He quoted Horace familiarly, and he has told us that he soon recovered his Greek when he began to decipher the Alexandrine MSS. on Alchemy.

His school studies over, he made up his mind to pursue natural science as a career, and he even mapped out a programme for the methodical study of the principles of *all* branches of science in what he afterwards called the "naïve confidence of youth." But, however much he may have had to curtail his educational ambition, he completed during the next few years a full medical course, he studied chemistry in the laboratory of Pelouze, and passed the University examinations for Bachelor and Licencié-ès-Sciences. To carry out this programme he took a small lodging in the Rue de l'Abbé-de-l'Epée, and attended the school of M. Crouzet. In this school happened that fortunate meeting between Berthelot and Ernest Renan—the beginning of a friendship which became from that day a principal element in the lives of both. Renan, then twenty-two, had renounced his clerical orders, and retired from Saint-Sulpice. Lonely and depressed by his mental struggles, he had become an assistant master in the school, but could not shake off his melancholy. Berthelot spoke to him, the talk became intimate, something in each ardent nature was touched and responded, and the two were drawn together until soul reacted with soul like acid and alkali. "Our friendship," wrote Renan, "was something analogous to that of the two eyes when they fix upon the same object, and from the two images there results a single impression in the brain." Renan and Berthelot would take long walks together, and on Sundays would visit Neuilly, then in the country, where Berthelot's parents had taken a house, and always they discussed the eternal problems that torture the human mind. One day Renan called his young friend a "Revolutionist." But Berthelot had one sure faith, built on the ruins of other beliefs. "I a Revolutionist," he cried, "clear your mind of that notion; call me rather an 'Evolutionist.'" We must remember that this was said a decade before Darwin gave us the "Origin of Species."

The ideas resulting from their stimulating intercourse took different shapes in the two minds, and though Renan admitted his indebtedness to Berthelot, it is impossible for us, as it was for them, to separate what was due to each. On the monument of Berthelot

which is to be placed in the Gardens of the Luxembourg, the sculptor, Saint Marceau, has introduced the face of Renan as a memorial of one of the most notable friendships of our time.

Under Pelouze the experimental skill of the young chemist rapidly developed, and in 1850 he presented his first paper to the Academy of Sciences—"On a simple method of demonstrating the liquefaction of gases." He showed how the gases chlorine, ammonia, and carbon dioxide could be liquefied in the capillary end of a glass tube by the expansion of mercury filling the body of the tube. When oxygen and nitric oxide showed no sign of liquefaction under pressures of 700 to 800 atmospheres he rightly concluded that under certain conditions of temperature it was not possible to liquefy gases by pressure alone. A second paper appeared in the same year, and in January, 1851, Berthelot received his first appointment, that of lecture-assistant to Balard, the discoverer of bromine, then Professor of Chemistry in the Collège de France. Unluckily the stipend was not a living wage—800 francs (£32) a year—and to earn a living Berthelot had to give private lessons. Luckily the official duties of the post were not heavy, and the resources of the laboratory were placed freely at his disposal by Balard, who in proposing him for the post wrote: "Everything allows us to hope that M. Berthelot will know how to utilise for the advancement of science the position I ask for him." In three years from his appointment Berthelot had obtained his doctorate by his remarkable thesis, "On the combinations of glycerine with acids, and on the synthesis of the immediate principles of animal fats." A year later he began to publish his work on the sugars, and the same year (1855) made the memorable syntheses of ethyl alcohol from ethylene, and of formic acid from carbon monoxide, which revolutionised the accepted ideas on the formation of organic compounds. Then followed in quick succession researches on the synthesis of hydrocarbons, of methyl alcohol, and of oxalic acid. After eight years' brilliant work, Berthelot was appointed Professor in the Ecole Supérieur de Pharmacie, where he lectured, but he continued to act as assistant and to research in the Collège de France. This was the first public recognition of his discoveries. Early in the following year (1860) this Society honoured itself and him by electing him a Foreign Member. At the invitation of Alexander Williamson, then President, Berthelot lectured before the Chemical Society, "On the synthesis of organic substances," on June 4th, 1863. It is pleasant to think that our Chemical Society set, rather than followed, the fashion.

With the appearance of his first book, "Organic Chemistry founded on Synthesis" (1860), the fame of Berthelot quickly spread.

The Jecker Prize was awarded to him in 1861 by the Academy of Sciences. The professors of the Collège de France, headed by Balard, petitioned the Minister of Public Instruction to found a Chair for Berthelot, and this movement resulted in his being appointed to a Professorship in the College in 1861, and finally (in August, 1865) in the formation of a special Chair of Organic Chemistry, which Berthelot held until his death. But though his early academic promotion was slow, honours came thickly to him in his middle age. The French Academy of Medicine elected him a member in 1863; he was elected to the Academy of Sciences in 1873, and of this body he succeeded Pasteur as Perpetual Secretary in 1889. In 1900 he became one of the forty French Academicians.

I cannot attempt any enumeration of the various learned societies of which he became an honorary fellow; I will only mention that he was elected a foreign fellow of our Royal Society in 1877, and that a Davy Medal was awarded in duplicate to him and to his friendly rival in thermochemistry, Julius Thomsen, in 1883, and that he received the Copley Medal, the highest distinction the Royal Society has to bestow, in 1900.

On his appointment to a Professorship in the Collège de France, Berthelot was enabled to fulfil his engagement to Mademoiselle Sophie Caroline Niaudet, niece of M. Louis Breguet, a French Swiss, whose family had been prosperous manufacturers of scientific instruments for many years, and who himself was the constructor of a well-known telegraph and induction coil. The story goes that the Berthelot and Breguet families had been intimate for some years, but Marcelin had not lifted his eyes to the beautiful Mademoiselle Sophie until one day accident brought them into collision on the Pont-Neuf. She was crossing the long bridge in front of Berthelot, and making her way with difficulty in the teeth of a strong wind, when a stronger gust catching her skirt and Tuscan hat blew Mademoiselle round into the arms of her future husband.

They were married on May 10th, 1861. Never was a happier match, or a more devoted family than Berthelot's. Madame Berthelot was endowed above most women with grace, with tact, and with sympathy; she brought into his life that great gift of serenity which Berthelot regretted he had not inherited from his mother. Well might he have appreciated our homely English saying, "It's an ill wind that blows nobody any good."

Busy in his laboratory by day and in his study by night, Berthelot took little part in public life under the imperial régime until the overthrow of Louis Napoleon and the siege of Paris in 1870. Then he threw himself whole-heartedly into the work of resisting the

invaders, and as president of the Scientific Committee of National Defence superintended the manufacture of explosives to be used against the enemy. After the war Berthelot continued the study of explosives, to which he applied all his experimental skill and the knowledge he had acquired in his thermochemical researches. In collaboration with Vieille he began a systematic investigation of the phenomena of explosions, which finally resulted, not only in the invention of a powder that gave to French arms for some years a remarkable superiority, but in the addition to science of a new chemical constant—*l'onde explosive*.

His work on the combination of nitrogen with organic bodies under the influence of the silent electric discharge turned his attention to the fixation of nitrogen by plants in the soil; in 1884 a laboratory was built for him on the heights of Meudon, and here he devoted himself every summer to problems of vegetable chemistry. Determined to take his share in the government of his country, he was elected a Permanent Senator in 1881, and in 1886 became Minister of Public Instruction in the Cabinet of M. Goblet. Here he found the opportunity of impressing on his generation his strong convictions on the educative and liberalising power of science. But he was no advocate of an illiterate mechanical training; he held firmly that science should be taught on the sound basis of a literary culture. It was in this spirit that he met the demand for "technical education" which swept over Europe. Industry demands two things, according to Berthelot: capable directors and competent workers. To be capable the director must be a judge of men and a judge of things; he must be trained in literature, history, and science; the high school and the university will prepare him for his business. To be competent the worker must be intelligent and skilful; the elementary school and the workshop will fit him for his job. Berthelot saw no need for ordinary technical schools—except as evening schools to help the workman. Can we yet say that Berthelot was wrong? At all events, he knew what he wanted, and he helped France to get it.

In 1895 Berthelot accepted the Portfolio of Foreign Affairs in the Bourgeois Cabinet. In this difficult post he had to negotiate the Anglo-French treaty dealing with the status and boundaries of Siam, which found herself in the uncomfortable position of "buffer" state between the French in Annam and the English in Burmah. Berthelot did not feel the duties of the Foreign Office congenial, and he resigned shortly after signing the treaty with Great Britain. But this, I think, we can say—that as a politician he had a sincere regard for England, and had he continued to guide the foreign relations of France the *Entente*, that has happily smoothed away

so many difficulties between the two nations, might have blossomed a decade earlier.

That Berthelot was a man of peace is evident from his book, "Science et Libre Pensée." It contains a strong plea for international arbitration. Of his other books mention must be made of his studies of the Greek and Arabian alchemistic writings. In 1869 Berthelot visited Egypt, where his imagination was struck with the early records of chemical and metallurgical experiments and ideas. He returned to this subject later, and followed it up with his characteristic eagerness. By his influence he obtained the publication of many rare manuscripts on alchemy, which he edited in collaboration with M. Ruelle, "Collection des Alchimistes Grecs," and with MM. Duval and Houdas, "La Chimie au Moyen-Age."

Few more interesting chemical papers have ever been published than the hundred and one preparations and recipes comprised in the Papyrus of Leyden translated by Berthelot. They reveal some of the methods of the Egyptian priesthood, who were the holders of the secrets of chemistry. How pithily is described the conversion of a copper vessel into a beautiful vase of gold (by rubbing it with gold amalgam and heating)—a vase which will stand the regular test of the touch-stone! With what cynical pleasure Berthelot remarks that such a fraud was no doubt quite natural, and even commendable in the eyes of a priest!

In 1880 it was my great privilege to be introduced to Berthelot in his laboratory at the Collège de France by Sainte-Claire Deville and Alexander Williamson. I had just been showing for the first time non-explosive mixtures of dried carbon monoxide and oxygen at the British Association Meeting at Swansea. Deville was enthusiastic over the discovery since it upset one of our cherished ideas; but Berthelot was more philosophical. Carbon monoxide was a gas, he said, "a little capricious" in its ways. One must repeat and again repeat such experiments. Most sound advice! I had, by the way, been repeating these experiments for four years before I published them; and it was in "again repeating" them that, all unconsciously, I struck across one line of Berthelot's own work—the measurement of the rate of explosion in gases.

But except for this natural attitude of philosophic doubt Berthelot was kindness itself. We were taken to his home in the Institute, and were entertained by Madame Berthelot, whose silver hair heightened the saint-like beauty of her face. Berthelot was full of fire and quick replies. When Williamson rallied him on the rapidity with which his memoirs appeared, Berthelot replied, "Ah! you English are too cautious, too frightened of committing your-

selves; what is worth doing is worth publishing!" It was perhaps characteristic of him that an hour before he had given me the opposite and better advice.

Those who met Berthelot in his prime could not but be struck with the intellectual sincerity and the intense enthusiasm of the man. The broad forehead, the brilliant, blue eyes, the clean-cut features, and the thoughtful expression impressed all who saw him; while his musical voice and clear enunciation charmed the ear. It would be impossible to forget that first impression.

Students who attended his lectures speak in the highest terms of the inspiration they drew from his teaching. He gave of his best, and delighted to show his audience the new experiments he was engaged upon. But it was when he forgot the immediate experiment in hand, and began to think aloud, that the inspiration was highest. Here truly was science "in the making."

(2) *His Scientific Work.*

In considering the amazing output of scientific work we owe to Berthelot, it would be useless to enumerate, and hopeless to discuss individual memoirs. Luckily they can be grouped into well-marked divisions, for Berthelot always followed up a train of thought until some logical explanation was reached that satisfied his mind. Then some idea suggested by the first research was followed up experimentally until another generalisation was reached, and other trains of thought could be pursued.

Study of Glycerine.—As soon as he was installed in Balard's laboratory in the Collège de France, Berthelot took up a line of research which led him on to discoveries of the highest interest. He began to study the modes of combination of glycerine with acids, and proved that it was an alcohol capable of combining with acids, to form "etherial salts"—thus bearing out the views of Chevreul that fats were "compound ethers," and justifying the modern name "glycerol"; but he also showed that glycerol differed from ordinary alcohol by its ability to combine with three equivalents of an acid instead of with one, just as phosphoric acid differs from nitric acid in combining with three equivalents of a base. By what seems a curious mental slip Berthelot likened the three classes of esters formed by glycerol to ortho-, para-, and meta-phosphates, instead of to their true analogues, the three salts of ortho-phosphoric acid. Wurtz not only made the correction, but by his synthesis of glycol —the "diatomic" intermediate between the "monatomic" alcohol and the "triatomic" glycerol—confirmed the importance of Berthelot's discovery. The work of Berthelot and Wurtz on the

polyatomic alcohols must rank in importance with that of Liebig on the organic polybasic acids. I think also, it is clear that the analogies shown by alcohols to inorganic bases—and I may specially mention the analogy between glycerol and bismuth hydroxide pointed out by Odling—led to the general adoption of the idea of valency which had been given to chemistry by Edward Frankland. The proof that glycerol is an alcohol led Berthelot to prepare and examine many other bodies of a like nature. We are indebted to Berthelot for a considerable number on the list of substances recognised as alcohols, and we constantly employ his method of acetylisation as the means of recognition.

Synthesis of Organic Substances.—I can only make a passing mention of very few of the many compounds of glycerol prepared by Berthelot by submitting it to the action of acids. Hydriodic acid, he found, yielded two substances, *iso*propyl iodide and allyl iodide; from the latter he made for the first time artificial oil of mustard.

The curious reducing power of hydriodic acid, especially at a high temperature, he afterwards made good use of in reducing benzene- to hexane-derivatives (1867). But the most stimulating thing to Berthelot's mind was the discovery that glycerol would combine, if time were given it, with all sorts of different acids, producing new fatty bodies, and that one could predict the formation of an endless number of new structures through a "creative power greater than that realised in nature." This idea, once planted in his mind, grew apace. He sought and found methods for preparing the simpler types of organic compounds, and from these to pass on to the higher and more complicated. To appreciate the boldness of Berthelot's conceptions we must remember the firm conviction that chemists held throughout the first half of the last century, that there was a gulf fixed between inorganic and organic substances; the chemist might build up, or synthesise, inorganic salts, but he could only break down, or analyse, the substances created in plants and animals by the "vital force." This gulf had not been really passed in the eyes of most chemists by the synthesis of urea by Wöhler or the formation of acetic and propionic acids from their nitriles by Kolbe and Frankland, for the cyanides from which these substances were formed were regarded as organic products themselves.

Berthelot's first success on his new path came in 1855. He shook up pure sulphuric acid in a large globe holding 32 litres of ethylene gas until 30 litres of the gas had been absorbed. The liquid was then mixed with water and distilled. The liquid coming over was dried and redistilled until 45 grams of a liquid having all the

properties of pure alcohol were obtained. But the original ethylene had itself been obtained from alcohol—so the synthesis might be said to be contaminated at its source. Berthelot next prepared ethylene iodide from coal gas, and from this prepared a sample of ethylene, which he treated as before. It yielded alcohol, which was thus made for the first time without fermentation.

Now since ethyl alcohol on heating with sulphuric acid yields ethylene and water, and formic acid on heating with sulphuric acid yields carbon monoxide and water, if the first process can be reversed, it might be predicted that the second would also:

$$C_2H_6O = C_2H_4 + H_2O.$$
$$CH_2O_2 = CO + H_2O.$$

Berthelot placed 10 grams of potash in a half-litre flask, which he filled with carbon monoxide, sealed, and heated for three days on a water-bath. When the flask was opened under mercury the gas was found to be completely absorbed; on dissolving the potash salt in dilute sulphuric acid and distilling, Berthelot obtained a distillate of formic acid.

In the following year (1856) a more difficult synthesis was effected —that of marsh gas, together with ethylene and acetylene. Formic acid on heating yields all its carbon as carbon monoxide and its hydrogen as water; but if there is present a strong base, which might cling to some of the carbon, a substance containing carbon and hydrogen might be evolved. Berthelot prepared formic acid on a large scale from carbon monoxide, combined it with baryta, and distilled the barium formate at a red heat. He condensed a small amount of liquid, caught the unsaturated hydrocarbons in bromine, and collected the marsh gas over water. The unsaturated hydrocarbons were ethylene and propylene. On decomposing their bromides by means of water and copper foil in thick glass tubes at 275°, Berthelot regenerated the ethylene and propylene, and found about 10 per cent. of acetylene—the result of a secondary action. From this ethylene he again prepared pure alcohol.

Berthelot's next starting point was carbon disulphide. If carbon disulphide were heated with a metal capable of combining with the sulphur, while at the same time hydrogen were liberated in contact with the nascent carbon, the two might combine to form a hydrocarbon. Passing hydrogen sulphide and carbon disulphide vapour through a broad tube packed with copper turnings freshly reduced and heated to a dull red heat, Berthelot condensed a trace of naphthalene, and collected ethylene in bromine and marsh gas over water. Iron acted in the same way as copper, and hydrogen phosphide and steam could be used instead of hydrogen sulphide.

Berthelot regenerated the ethylene as before (finding acetylene produced), and prepared alcohol from it. One cannot help feeling in reading Berthelot's account of this experiment that in his mind the ethylene (with its resulting alcohol) was more important than the marsh gas. But a year later Berthelot chlorinated marsh gas in diffused daylight, separated the methyl chloride from the residual marsh gas and higher chlorides by solution in anhydrous acetic acid, and prepared methyl alcohol from the chloride.

Just as Berthelot had got ethyl alcohol from ethylene and sulphuric acid, so he obtained propyl alcohol from propylene and sulphuric acid. The propylene was prepared from the propyl iodide obtained from glycerol and phosphorus iodide. Again he showed that the higher olefines could be combined with hydrogen chloride and the chlorides turned into the corresponding alcohols—a general method by which he prepared many alcohols; and *vice versâ*, by abstracting the elements of water the olefines could be prepared from the alcohols. Again, as barium formate yielded on distillation several hydrocarbons, so might the acetate of sodium yield other hydrocarbons than marsh gas. Berthelot found that it yielded higher olefines as well, namely, propylene, butylene, and amylene.

But among the most memorable of Berthelot's syntheses was the direct combination of hydrogen and carbon in the electric arc to form acetylene (1862), and the condensation of acetylene into benzene (1866); thus the barrier between inorganic and organic chemistry was broken down at all points, and Berthelot's disciples could exclaim with justice: "There is but one chemistry, and Berthelot is its prophet."

In working on acetylene Berthelot investigated the properties of the acetylides of silver and copper. This work led him in 1866 to make the suggestion that the mineral oils found in the earth might have been formed from acetylene produced by the action of water and carbonic acid on the acetylides of the alkali metals. By reducing the carbonaceous matter found in meteorites he produced some liquid petroleum.

Action of Heat on Hydrocarbons.—Berthelot's work on the hydrocarbons included a study of the mode in which these bodies behave at a red heat. A hydrocarbon, he says, is not directly resolved into its elements, but either polymerises (for example, acetylene into benzene) or by a condensation of two or more molecules forms a denser hydrocarbon with elimination of hydrogen; thus marsh gas gives mainly acetylene and hydrogen, ethane yields ethylene and hydrogen, while ethylene yields mainly acetylene and hydrogen. Acetylene itself is not resolved into its elements, but polymerises,

or condenses with hydrogen or other hydrocarbons into compounds of great density—naphthalene, anthracene, etc. When carbon is finally separated, it is therefore not a simple molecule, but in the form of a highly complex group of atoms corresponding with the dense hydrocarbons yielding it. This attractive theory of Berthelot has not, however, been fully borne out by later work. Sir Edward Thorpe showed that the decomposition of a paraffin (under heat and pressure) gave rise to the formation of an olefine and a lower paraffin; and Haber showed that *n*-hexane gave methane and amylene, but confirmed Berthelot's observation that benzene condensed to diphenyl with loss of hydrogen. Bone and his colleagues have shown that methane is formed directly from its elements between 1000° and 1200°, and breaks up again into carbon and hydrogen without forming acetylene. Ethylene, on the other hand, gives acetylene, which itself can either recombine with hydrogen or break down into carbon and hydrogen.

Action of Mass.—The observation made by Berthelot that time was required for the union of glycerol with acids led him, in conjunction with his pupil, Péan de St. Gilles, to investigate the course of the reaction between alcohols and acids, especially that between ethyl alcohol and acetic acid. Here, again, Berthelot was a pioneer in a subject that had hardly been touched experimentally. He found that when equivalent amounts of alcohol and acid are brought together, the reaction proceeds slowly (at a rate depending on the temperature) until a limit is reached, and that the same limit is reached when the corresponding amounts of ester and water are brought together. "An equilibrium is established between the affinity of the acid for the alcohol, which tends to unite them, and the inverse affinity of the water for the neutral ether, which tends to regenerate the acid and the alcohol." We can put the result into an equation:

$$\frac{C_2H_3O_2 \cdot C_2H_5 \times H_2O}{C_2H_4O_2 \times C_2H_6O} = 4.$$

It is clear, I think, that Berthelot regarded the equilibrium as a statical, and not as a dynamical, one; he did not see that the two opposite reactions were taking place at the same time; Guldberg and Waage recognised this, and used Berthelot's figures in illustration of their principle. Nevertheless, Berthelot and St. Gilles' memoirs form the starting points of much of the subsequent work on equilibrium and mass action. They showed the effect on the equilibrium of varying the amounts of one of the reacting substances; they showed that an increase of temperature or of concentration greatly shortened the time for the equilibrium to be

reached, although pressure alone had little effect. They suggested an equation for the determination of the velocity of a bimolecular reaction similar to that of Harcourt and Esson. Few researches indeed have been more fruitful in physical chemistry than those of Berthelot and St. Gilles.

Of other equilibrium problems Berthelot was the first to investigate the partition of a dissolved substance between two solvents. He showed, for instance, that when succinic acid is dissolved in ether and water, the coefficient of distribution is constant whatever the amounts dissolved; but other substances showed a variation with concentration, an anomaly explained by Nernst in 1891 as due to a difference of the molecular aggregation of the substance in the two solvents. In 1875 Berthelot studied the partition of acids between several bases in solution.

Thermochemistry.—Berthelot's great work on thermochemistry was begun in 1863, and was continued until 1879, when he published the two volumes entitled, "Mecanique Chimique fondée sur la Thermochimie." This and his later book, "Thermochimie, Données et Lois numériques," constitute a monument of elaborate experiment and calculation, which men of science rank alongside the "Thermochemische Untersuchungen," the life-work of Julius Thomsen. It is not at all to the disadvantage of Chemistry that the Frenchman and Dane worked in rivalry. When we want to know the heat of formation of any compound we look up the two authors, and if they agree we are entirely satisfied. I think each respected the other's work. I can point to an instance—the heat of formation of ammonia—where Thomsen corrected his first result, and to another—the heat of formation of ethane—where Berthelot corrected his; in each case as the result of the other's work. They both put forward a theorem, though not quite in the same terms, that every action of a purely chemical nature gives out heat and produces the result that is accompanied with the maximum evolution of heat. Berthelot defended with great skill his "principle of maximum work"; it required the genius of Helmholtz and Boltzmann to prove that the principle required that the heat of reaction should be independent of the temperature, and was only strictly true at absolute zero. But although these limitations must be accepted, and Berthelot finally accepted them, the "law" is nevertheless a useful guide which is often appealed to. Was not Deacon inspired by Berthelot's ideas when he sought and finally found a practical method of liberating chlorine from hydrochloric acid by the oxygen of the air?

Much of the apparatus devised by Berthelot for his thermo-

chemical determinations has come into general use; in particular, I may mention his "calorimetric bomb" for combustions in oxygen under pressure.

Explosions.—Berthelot's experiences in the war led to his systematic work on explosives and on the theory of explosions. In conjunction with Vieille he studied the rapidity of combustion and the heat of reaction of various explosives. In July, 1881, he published his first short paper on the explosion-wave in gases. He states that he would not have published it had not MM. Mallard and Le Chatelier sent him their memoir on the same subject, which they had attacked by a different method. It is a curious coincidence that a few months before I had myself begun to measure the rate of explosion of carbon monoxide and oxygen with different quantities of water-vapour, and found that the accepted rate was altogether too slow.

Berthelot's first paper contains the germ of his theory—the identity of the rate of explosion with the mean velocity of the molecules formed in the reaction before any heat had been lost. Other papers quickly followed. Berthelot made the important discovery that the rate of explosion rapidly increased from the point of origin until it reached a maximum which remained constant, however long the column of gases might be. This maximum Berthelot stated to be independent of the pressure of the gases, of the material of the tube, and of its diameter above a small limit. The rate of explosion thus forms a new physico-chemical constant, having important theoretical and practical bearings. The name "l'onde explosive" was given by Berthelot to the flame when propagated through an explosive mixture of gases at the maximum velocity, and this velocity could be predicted if the heat of combination and the density and specific heat of the products were known. For instance, the total heat given out when hydrogen and oxygen combine is known. If this heat is contained in the steam produced, its temperature may be calculated if its heat capacity be known; and if the temperature of the steam be known, the mean velocity with which the molecules must be moving can be calculated. Now Berthelot supposed that the heat is all contained in the steam produced. He assumed that the heat capacity of steam was the same as the sum of those of its constituents; and he supposed, moreover, that the steam was heated at constant pressure. Making these assumptions, he calculated out the theoretical mean velocity of the products of combustion of various mixtures, and found a close accordance between these numbers and the explosion rates of the same mixtures. He concluded that the explosion-wave was propagated by the impact of the products of combustion of one layer

upon the unburnt gases in the next layer, and so on to the end of the tube at the rate of movement of the products of combustion themselves. If this theory be true, it accounts, not only for the extreme rapidity of explosion of gaseous mixtures, and gives the means of calculating the maximum velocity obtainable with any mixture of gases, but it also affords information on the specific heats of gases at very high temperatures, and explains the phenomena of detonation whether of gases or of solid or liquid explosives.

Table I shows the explosion rates found by Berthelot, compared with the theoretical velocity of the products of combustion:

TABLE I.

Gaseous mixture.		Velocity in metres per second. Calculated.	Found.
Hydrogen and oxygen	$H_2 + O$	2830	2810
Hydrogen and nitrous oxide	$H_2 + N_2O$	2250	2284
Carbon monoxide and oxygen	$CO + O$	1940	1090
Carbon monoxide and nitrous oxide	$CO + N_2O$	1897	1106
Marsh gas and oxygen	$CH_4 + O_4$	2427	2287
Ethylene and oxygen	$C_2H_4 + O_6$	2517	2210
Cyanogen and oxygen	$C_2N_2 + O_4$	2490	2195
Acetylene and oxygen	$C_2H_2 + O_5$	2660	2482

Two facts established by these experiments impressed on me the conviction that Berthelot might have found the true theory of explosions: first, the close coincidence between the rates of explosion of hydrogen (both with oxygen and nitrous oxide) and the calculated mean velocities of the products of combustion; and, secondly, the great discordance between the found and calculated rates for carbonic oxide with both oxygen and nitrous oxide, for I had previously discovered that pure carbon monoxide cannot be exploded either with pure oxygen or pure nitrous oxide. The discordance found by Berthelot was what I should have expected from my own experiments. Again Berthelot examined the effect of inert gases in damping down the velocity of the explosion-wave; for instance, on adding nitrogen to different explosive mixtures he found:

TABLE II.

Gaseous mixture.	Velocity in metres per second. Calculated.	Found.
$H_2 + O$	2831	2810
$H_2 + O + N_2$	1935	2121
$H_2 + O + 2N_2$	1820	1439
$CH_4 + 2O_2$	2427	2287
$CH_4 + 2O_2 + 2N_2$	2002	1858
$CH_4 + 2O_2 + 4N_2$	1744	1151
$C_2N_2 + 2O_2$	2490	2195
$C_2N_2 + 2O_2 + N_2$	2334	2044
$C_2N_2 + 2O_2 + 2N_2$	2152	1203

These experiments seemed to Berthelot to show that a small amount of inert gas does not prevent the propagation of the true explosion-wave, but damps it down according to its calculated effect. A large amount of inert gas, on the other hand, destroys the character of the explosion-wave—which must always be regarded as the "*maximum possible*" velocity.

In comparing the rates of explosion determined in his tube with those calculated from his formula, Berthelot, I think, was not justified in his argument that the specific heats of the gaseous products must be reckoned as at constant pressure, since the whole change took place in a closed tube. In the damping experiments with nitrogen he did not allow for the fact that with inert gases a longer run is required before the explosion-wave is set up, and he began to time the flame before it had acquired its maximum pace. In the cyanogen experiments he did not appreciate the fact that in the wave-front the carbon only burns to carbon monoxide. But in spite of these criticisms, which required years of work to establish, I have always thought it one of Berthelot's strokes of genius to identify the maximum velocity of the flame with the mean translational velocity of the molecules themselves, a conception which all later investigators have used in working out the propagation of an intense pressure-wave which preserves its type by being continually reproduced from point to point by the chemical action.

Fixation of Atmospheric Nitrogen.—In Berthelot's synthetic researches we find him using the silent electric discharge to cause nitrogen to enter into combination, for example, as in the direct formation of hydrocyanic acid from acetylene and nitrogen. This fixation of nitrogen led him to investigate its absorption by plants, and generally the action of electricity on vegetable growth in his laboratory at Meudon. Berthelot asserted that free nitrogen could be assimilated by plants, a statement that was vehemently opposed until Hellriegel proved that leguminous plants can take up nitrogen through the agency of bacteria. Berthelot was the first to point out that atmospheric nitrogen was fixed in the soil by micro-organisms, a new departure of supreme interest to agriculture. Among other developments of Berthelot's idea, Dr. E. J. Russell has recently shown how the fertility of a soil might be enormously increased by killing off the infusorial enemies of these bacteria. Four solid volumes, entitled, "La Chimie végétale et agricole," published in 1899, contain the record of Berthelot's work at Meudon.

Looking back at the enormous mass of experimental detail published by Berthelot I am astonished at the small percentage of

error that has been detected. The accuracy of his experiments is really marvellous. It is not in his experiments, but in his interpretation of them that Berthelot has to meet criticism. Although Berthelot was a rapid worker, he was a still more rapid thinker. Not once or twice, but almost throughout the range of his researches we see the theoretical conception outstripping the experiment. Sometimes deliberately, sometimes unconsciously, he chooses his experiments to illustrate his theory. It is a question of idiosyncrasy; genius must work its own way. The nineteenth century praised Dalton for basing his Atomic Theory on the sure foundation of the Law of Multiple Proportions; the twentieth century knows that Dalton sought for cases of multiple proportion to support his preconceived theory of atoms.

Berthelot's imagination gives a distinction to all his work; his rapidity of generalisation fascinates us, and compels our interest. Can we say which is the better for knowledge—on the one hand, the dashing advance of an explorer into an unknown country, the rapid survey, the approximate location of a great lake and a great mountain range, and the publication of a fascinating sketch-map giving us the possible sources of a Nile or a Congo; or, on the other hand, the deliberate advance of a surveyor with his levels and theodolites? May it not with justice be maintained that had it not been for the pioneer and his map the surveyor would never have started at all? Berthelot might rightly claim that he had pointed out the trend of the country and the possibilities that lay that way, and had stimulated the curiosity of the exploring world. "For myself," he wrote, "I shall be happy if, in the development of science, some of my results are valued some day as the origin of the discoveries of the future." I believe this was no conventional phrase of self-depreciation, but an expression of his thought used in all sincerity.

Again, like other great men, Berthelot found it hard, even when the creatures of his thought had been proved to be "unemployables," to dismiss them from his service. I ventured just now to compare Berthelot's mode of thought with Dalton's. May we extend the parallelism further, and say that the intensity of conception in the mind of each was sometimes too strong to yield to facts? Dalton, firm in his conviction that different elements had atoms of different sizes (the very genesis of his theory), could see neither the relevancy of Gay-Lussac's Law of Volumes nor the beauty of Avogadro's explanation. For him the formula of water was always HO. Berthelot, equally firm in his conviction that in chemical reactions we are dealing with "equivalents," could see the force of Gay-Lussac's experiments, but not of Avogadro's argument. For him

the formula of water (the molecule occupying 2 volumes) was H^2O^2.

If we, then, as the result of the steady progress of experiment and thought, can see the limitations of Berthelot's vision, we can also, I hope, appreciate the brilliancy of the conceptions that guided his work, and the intensity of the stimulus given by his ideas to contemporary science.

(3) *The Last Phase.*

Berthelot enjoyed a wonderfully active and honoured old age. To celebrate his seventy-fifth birthday and the jubilee of his first appointment in the Collège de France, his colleagues inaugurated a great meeting of congratulation, and commissioned M. Chaplain to design a medal in his honour.

The Chamber of Deputies and the Senate declared that the occasion demanded a public ceremonial, in which the State should participate. Abroad, all the great societies passed resolutions congratulating Berthelot on his achievements, and sent delegates to present their felicitations in person. The meeting was held in the great hall of the Sorbonne on November 24th, 1901. Berthelot declined the procession and the military escort offered by the State, and went on foot to the hall. He was received by the President of the Republic. Then amid the acclamation of his colleagues, who thronged the hall, he heard perhaps for the first time from the mouths of his most distinguished contemporaries the deep veneration in which the world held his genius and his career. In acknowledging this great demonstration, Berthelot once more insisted on the humanising spirit of science. "It is not," he cried, "for the satisfaction of our private vanity that the world to-day pays homage to men of science. No! it is because it knows that the man of science really worthy of the name consecrates his life disinterestedly to the great work of our age—the amelioration of the lot of all, the rich and the happy, the poor and the suffering. It is this that my friend Chaplain has sought to express on the beautiful medal which the President of the Republic is to offer me. I know not if I have completely fulfilled the noble ideal the artist has drawn, but at least it has brought me strength to have made this the aim that has directed my life."

"*Pour la Patrie et la Vérité*"—the design was well chosen by Chaplain to sum up Berthelot's career.

Berthelot continued to work to the end. Although he ceased to lecture, he seldom passed a day without visiting his laboratory. There and in his home he found his happiness, for husband and wife seemed to grow nearer as the years went by. In his last months

he had the sorrow of losing a daughter and then a beloved grandson. The shock preyed on his wife, who developed heart disease. Berthelot, himself a victim to the same disease, watched assiduously at her bedside, and wasted his strength in his nightly vigils over her. A Sunday came when she seemed better, and Berthelot visited his laboratory at Meudon, where he was studying the effects of radium emanations on vegetation. On his work table there was found afterwards an alchemic manuscript from Morocco, written in Hebrew, which he was deciphering, for he had not forgotten the early lessons he had received from Renan.

He returned to find his wife failing, and they both knew the end was near. "What will become of him when I am no longer there?" were the last words she spoke to her daughter. Berthelot was alone with his wife when she died. He called his children, kissed the dead, walked into the next room, and threw himself upon a couch. One of his sons followed him, and hearing him sigh, ran to seize his hand. But the hand was lifeless: he had joined his beloved one.

The pagan poet whom Berthelot loved has perhaps made us feel most keenly the cry of the heart that cannot survive separation:

"Ah! te meae si partem animae rapit
Maturior vis, quid moror altera,
Nec carus aeque nec superstes
Integer? Ille dies utramque.

Ducet ruinam. Non ego perfidum
Dixi sacramentum. Ibimus, ibimus
Utcumque praecedes, supremum
Carpere iter comites parati." *

The state procession and military escort which Berthelot had declined alive were fitting attendants round the hearse that bore the bodies of husband and wife to honourable sepulchre in the Pantheon.

So passed away a great man, full of years and honour. To France and to Science he gave his life, and he was not without reward in the love and veneration of his countrymen. Happy the country that produces such genius; happier still the country that can appreciate and use it.

* At the request of the Publication Committee, I subjoin the English renderin of these stanzas I gave at the Lecture:

"If Death, untimely, snatch away
That half—ah! dearer half—my soul,
Why should this other half delay?
Could life be sweet no longer whole?

The day that strikes thee strikes us both:
Together, when thou goest, we go
Sworn comrades ('tis no idle oath)
To tread the last long path below."

—*Horace* II. xvii.

MOISSAN MEMORIAL LECTURE.

Delivered on February 29th, 1912.

By Sir William Ramsay, K.C.B., F.R.S.

France has always held one of the highest places among the nations in the brilliance and originality of her sons. In the domain of chemistry, especially, many names of illustrious Frenchmen suggest themselves; Lavoisier, Guyton de Morveau, Berthollet, Gay-Lussac, Dumas, and Berthelot stand out among a crowd of others hardly less distinguished. We have recently heard from the eloquent lips of our late President, Professor Dixon, a charming account of the life and work of the last named of these eminent men; it is my duty to-night to ask you to listen to a brief discourse on a contemporary of Berthelot's, who, though cut off by fate at a comparatively early age, stood only second to him among the representatives of chemistry in France in his time.

Henri Moissan was born in Paris on September 28th, 1852. His father was a native of Toulouse; his mother, whose maiden name was Mitelle, was of an Orleans family. Moissan's features and his bright, vivacious manner betrayed his southern origin; he was of the best French type.*

His education, after school life, began in the Collège de Meaux, and in his twentieth year he entered the laboratory of Frémy at the Musée d'Histoire Naturelle attending at the same time the lectures of Henri Sainte-Claire Deville and Debray. He made good progress, and after spending a year at elementary work he removed to the neighbouring laboratory of Decaisne and Dehérain, in the École Pratique des Hautes Études, with whom he worked on practical problems bearing on vegetable life. Whilst there, he passed the examinations required for graduation, taking the preliminary degree of Bachelier in 1874; of Licentié in 1877; in 1879 he became "Pharmacien de première Classe"; and in 1880 he qualified as "Docteur ès Sciences physiques."

After working with Dehérain for little more than a year, he left the Museum to direct a small laboratory of his own; and he then abandoned the study of vegetable chemistry for that of inorganic chemistry, a branch to which he remained faithful during the rest of his life, and in which he achieved the highest distinction. This

* Madame Moissan has had the kindness to place at my disposal the photographs and specimens exhibited during the lecture.

private laboratory was given up somewhat later; and he then found quarters with MM. Debray and Troost, in the laboratories of the Sorbonne, of which in after time he was to become Director.

In 1879 he was appointed "Répétiteur de Physique" at the Agronomic Institute, and after spending a year in that position he was promoted to the post of "Maître de Conférences" and "Chef des Travaux Pratiques," or lecture assistant and senior demonstrator at the École Supérieure de Pharmacie, a position which he held until 1883. A year before this change, he had been appointed, after a competitive examination, "Agrégé des Sciences physiques-chimiques," and his standing among his fellows at that date was such that on the death of Professor Bouis in 1886 he was elected to the Professorship of Toxicology in the School of Pharmacy; he retained that Chair until 1899, when his turn came in rotation to occupy the Chair of "Mineral" or Inorganic Chemistry; he then for the first time delivered a course of lectures on that branch of chemistry.

In 1900 he was appointed Assessor to the Director of that School, and in the same year, on the retirement of Professor Troost, the Professor of Inorganic Chemistry in the Faculté des Sciences in the University of Paris, Moissan was unanimously chosen as his successor, for his name had become very widely known owing to his remarkable discoveries. At the same time, he retained the title of Honorary Professor at his old school, the École de Pharmacie.

Moissan's first research was conducted in conjunction with Dehérain; it had reference to the interchange of oxygen and carbon dioxide in the leaves of plants which had been exposed to the subdued light of a darkened room.

His first work in the domain of inorganic chemistry dealt with the oxides of the iron group of metals, and especially with the compounds of chromium. His thesis for the doctorate contained an account of a portion of this research. In it he described the existence of two allotropic modifications of chromium sesquioxide; one obtained by igniting ammonium chromate, as well as by other methods, insoluble in acids, unattacked by hydrogen sulphide and by oxygen; the other, produced by careful drying of the hydrated oxide at 440°, which, when heated to 140° in a current of hydrogen sulphide, gave a black sulphide, Cr_2S_3, reducible to chromous sulphide, CrS, by further heating in a current of hydrogen. Oxygen converted this variety of sesquioxide into the analogue of manganese dioxide, CrO_2, a dark grey powder.

This train of thought led Moissan to investigate the products of reduction of the oxides of the iron group. The so-called "pyrophoric iron," obtained by heating ferrous oxalate, was shown to consist

of ferrous oxide, FeO; the same substance is produced by reducing the oxide, Fe_2O_3, in a current of a mixture of carbon dioxide and hydrogen. The action of hydrogen at 330—440° reduces Fe_2O_3 to Fe_3O_4, and the magnetic oxide is also formed by heating the sesquioxide in a current of carbon monoxide at the temperature of melting zinc. It is only at 500—600° that ferrous oxide is produced; it is pyrophoric at the ordinary temperature. But pyrophoric iron itself can be obtained by heating the sesquioxide for a long time in a current of perfectly dry hydrogen to 440°, or by distilling away the mercury from an amalgam of iron. The amalgam, indeed, prepared by electrolysing a solution of ferrous chloride with mercury as the cathode, turns very hot on exposure to air.

An allotropic variety of the magnetic oxide, Fe_3O_4, was produced by heating the monoxide, or metallic iron reduced by hydrogen, to redness in a current of moist hydrogen. It formed a black magnetic powder, incandescing and changing to Fe_2O_3 when heated in air. At 1500° Fe_2O_3 gave off oxygen, and was converted into a very resisting modification of the magnetic oxide.

Somewhat similar researches were carried out on the oxides of manganese, nickel, and cobalt, and pyrophoric varieties of the metals were prepared.

Having obtained metallic chromium from its amalgam, Moissan next investigated the little-known chromous salts, preparing pure chromous chloride, $CrCl_2$; also the blue sulphate, $CrSO_4,7H_2O$, which is isomorphous with copperas; also chromous bromide, chromous acetate, and chromous oxalate. The acetate or chloride, on treatment with a solution of potassium cyanide, gave the interesting compound, $K_4CrC_6N_6$, analogous to yellow prussiate of potash, oxidisable to the red $K_3CrC_6N_6$. A final paper on the blue compound of CrO_3 with peroxide of hydrogen, in which it was shown that the ratio between the two is CrO_3: H_2O_2, ends the series.

In 1884 Moissan turned his attention to the investigation of compounds of fluorine. He prepared phosphorus fluoride first, by heating copper phosphide with lead fluoride. It is a gas, exploding when sparked with oxygen, and yielding the oxyfluoride, POF_3. He next prepared fluoride of arsenic, by distilling a mixture of arsenious oxide, sulphuric acid, and calcium fluoride. He electrolysed this liquid, and produced from it elementary arsenic, and a gas which attacked the platinum electrode. On submitting phosphorus fluoride to a rain of sparks, phosphorus was deposited; the product, however, was not fluorine, but phosphoric fluoride, PF_5, the liberated fluorine combining with the phosphorus fluoride. These researches occupied him until 1888. In that year he investigated some organic fluorides, obtaining ethyl fluoride, C_2H_5F, by the

interaction of ethyl iodide and silver fluoride, and the corresponding methyl and *iso*butyl fluorides. In the following year he made the capital discovery that whilst the compound KF,2HF melts at 65°, KF,3HF remains liquid at −23°, and conducts electricity electrolytically; and this long series of researches culminated in the discovery of elementary fluorine.

During this work he accumulated useful information, which enabled him to adapt his apparatus to the end he had in view. One method which he attempted for the isolation of fluorine was to pass phosphorus and phosphoric fluorides over red-hot platinum sponge. A gas was evolved which liberated iodine from a solution of potassium iodide; but this gas came off very slowly, and was largely absorbed by the platinum tube in which the experiment was made. He next tried the electrolysis of arsenious fluoride; but he found that that liquid is a very poor conductor, and he attempted to increase its conductivity by the addition of anhydrous hydrogen fluoride; better results, however, were obtained on addition of anhydrous potassium fluoride to the mixture of arsenious fluoride and hydrogen fluoride; and from this it was but a step to omit the arsenious fluoride and to electrolyse the mixture of acid and potassium salt.

His first apparatus was made of platinum; the electrodes were rods of platinum-iridium alloy, thickened at the ends so as to last longer, for the negative electrode was always rapidly corroded. Paraffined corks closed the ends of his first platinum U-tube. The cork closing the limb into which the negative electrode passed was corroded and charred; hence in his next experiment, corks were replaced by fluor-spar stoppers, cemented into hollow platinum cases, on which a screw was turned, so that the stoppers could be screwed tight into the open ends of the U-tube. This experiment was successful in yielding fluorine; whilst hydrogen came off at the negative electrode, and passed out through a side-branch of platinum tube, fluorine was evolved at the positive pole; it passed out through a similar platinum tube, and was made to play on various materials exposed to its action in a platinum capsule. It was subsequently discovered that as copper exposed to fluorine immediately becomes covered with a deposit of the fluoride, which protects it from further action, copper could be substituted for platinum in the structure of the U-tube, and an important economy could thus be effected.

It was found that sulphur, selenium, and tellurium inflamed, giving white deposits; the first combines, as Moissan subsequently found, to form a gas, SF_6, sulphur hexafluoride. From phosphorus, PF_3 and PF_5 were obtained; iodine caught fire and burned; Moissan

subsequently found that IF_5 was the product; bromine lost its colour, and later, Moissan and his pupils proved this to be due to the formation of BrF_3; on pure carbon at the ordinary temperature fluorine had no action; but both boron and silicon caught fire and burned, giving SiF_4 and BF_3.

By blocking the exit of either of the tubes conveying away the hydrogen or the fluorine, one or other gas could be caused to pass round the bend and mix; when a bubble passed round, a detonation occurred, showing that hydrogen and fluorine combine even in the dark at the low temperature of $-35°$, for the apparatus had to be maintained at this low temperature to prevent the admixture of gaseous hydrogen fluoride with the fluorine. The low temperature was conveniently attained by surrounding the U-tube with liquid methyl chloride.

Most metals were instantly attacked, some with inflammation; even platinum and gold could not resist its action; but they had to be raised to 400° before attack took place. Salts such as potassium iodide, mercuric iodide, and lead iodide were completely decomposed, giving fluorides both of the metal and of the iodine. Chlorine was liberated from potassium chlorate, along with oxygen, on which fluorine had no action; chlorine was also evolved from carbon tetrachloride, the tetrafluoride being formed; and water was instantly decomposed, its oxygen being liberated partly as ozone.

Although all these properties of this gas could be most easily explained on the assumption that it consisted of fluorine, still they might conceivably appertain to a mixture of ozone and hydrofluoric acid, or to a perfluoride of hydrogen, HF_n. The former supposition was disproved by trying the action of such a mixture; but none of the properties of the gas was manifested. The second hypothesis was also disproved by leading the fluorine over iron, and proving that no hydrogen passed on.

Subsequent research showed that the formation of fluorine was not so simple as had at first been supposed. Investigation of a muddy deposit, which was always found at the bend of the U-tube on dismantling it, showed that that substance consisted mainly of potassium platinifluoride, K_2PtF_6, and that in all probability it was the substance undergoing electrolysis, the equivalent of the potassium being liberated at the cathode as hydrogen, and fluorine at the anode, the group PtF_4 again combining with potassium fluoride. The operation did not proceed with regularity until a considerable quantity of platinum had dissolved from the anode.

The density of the gas was found to be 18·3, on the hydrogen standard. This figure, which is too low, was almost certainly due to the presence of oxygen, produced by the electrolysis of water

still dissolved in the electrolytic mixture. Moissan for long supposed that, on passing the current, the water accidentally present first underwent electrolysis before the fluorine appeared; but it was subsequently found that water still remained to be electrolysed, even after much fluorine had been separated. Later experiments, in which the gases other than fluorine were estimated in the gaseous mixture, weighed, and allowance was made for their presence, proved that the true density of fluorine is 19, a figure identical with the atomic weight. The supposition that fluorine consisted partly of monatomic molecules mixed with an excess of diatomic molecules had therefore to be abandoned. The activity of fluorine was not to be explained by its monatomicity.

The reason why fluorine cannot be produced by heating tetrafluoride of platinum, PtF_4, was found as soon as that substance had been prepared by the action of fluorine on platinum; it is because that compound decomposes water, and therefore cannot be prepared in the wet way.

Moissan also attempted to induce combination between argon and fluorine, and helium and fluorine, but without success, even when the mixture was submitted to the discharge of powerful sparks.

The preparation of two gaseous fluorides of carbon led Moissan to attempt to remove the fluorine, in the hope that the carbon would be liberated in the form of diamond. But this hope was disappointed; the product was always lamp-black. These experiments, however, led to the discovery of the method of preparing the diamond artificially; it had been found that a meteorite from Cañon Diablo, consisting, as meteorites usually do, mainly of metallic iron, had imbedded in it small crystals of diamond; and Moissan's genius led him to devise the cause of their formation; his theory was that the carbon had originally been dissolved in the iron when it was in a molten state; that the surface of the iron had suddenly cooled, and that the iron in the interior, on solidifying, was subjected to great pressure, for solid iron containing carbon in solution occupies a larger volume than molten iron. These considerations directed his experiments, which were crowned with success.

His first experiments, however, in which the iron was saturated with carbon at about 1000°, were not successful; he accordingly argued that at higher temperatures the solubility of carbon in iron should increase, as is the general rule; and he devised the electric furnace to attain much higher temperatures. His three great investigations are thus seen to hang together; one suggested the other, and Moissan's skill and patience brought all to a successful

conclusion. The spirit in which he carried out his work is well expressed in his own words, which occur in the preface to his book on the "Electric Furnace": "But what I cannot convey in the following pages is the keen pleasure which I have experienced in the pursuit of these discoveries. To plough a new furrow; to have full scope to follow my own inclination; to see on all sides new subjects of study bursting upon me, that awakens a true joy which only those can experience who have themselves tasted the delights of research."

Moissan's electric furnace, designed not for technical, but purely for experimental work, was of the simplest construction. It consisted of a rectangular block of lime, made of the excellent Paris limestone, in the centre of which a hole had been scooped. This block was covered with a rectangular lid; two grooves of circular section admitted the carbon poles which served as electrodes, and an arc was made between the poles. Later, an electromagnet was used to deflect the arc downwards, so that it might play more directly on the object to be heated. A current of 100 to 125 amperes at 50 or 60 volts was employed in his earlier researches.

The volatilisation of the material of the furnace, lime, was the first fact to be chronicled. Indeed, two torrents of what appeared to be flame poured out through the holes admitting the electrodes. These apparent flames were, however, only white-hot lime dust, condensed from the lime-vapour which filled the furnace. Subsequently, to save cost, the body of the furnace was constructed of limestone. The crucible to be heated stood on magnesia, to avoid the rapid formation of calcium carbide; and for some purposes, crucibles were constructed of a grid of alternate slices of carbon and magnesia. By heating an inclined carbon tube in the arc, and feeding in at one end a mixture of an oxide such as chromium oxide and carbon, the metal flowed out at the other end, and a continuous supply was thus obtainable.

The temperature of the electric furnace appeared to depend on the quantity and intensity of the current; but it is limited, no doubt, by the temperature of volatilisation of carbon.

By help of this powerful engine of research, Moissan succeeded in causing many changes to occur, and in producing many compounds previously unknown. Some of these compounds have had important commercial applications; others are of great interest, owing to the reactions which they undergo, and the light that they shed on the problems of chemical combination.

In his systematic search for a method of producing artificial diamonds, Moissan investigated numerous varieties of graphite; he subjected different kinds of carbon to the intense heat of the

electric furnace, in order to study their behaviour, and, as before remarked, he studied the Cañon Diablo meteorite, in which small diamonds are embedded. These researches made him familiar with the behaviour of carbon in all possible circumstances, and enabled him to separate diamonds from other materials with which they might be mixed.

The first actual experiment of crystallising carbon under pressure from iron was made with 200 grams of Swedish iron, fused in the electric furnace for six minutes with sugar-charcoal in a carbon crucible. The crucible was then seized with tongs, and plunged into a vessel full of cold water. Moissan relates the anxiety with which this was first attempted; an explosion was feared; but, although the water boiled, no accident occurred then, or, indeed, during some hundreds of similar experiments. The iron was dissolved in dilute hydrochloric acid; the residue, chiefly consisting of carbon in various forms, was extracted with nitrohydrochloric acid, and alternately with boiling sulphuric and hydrofluoric acids. It was then, in order to remove graphite, boiled with nitric acid and potassium chlorate. The final residue was floated in bromoform, in which some transparent dust, of density 3 to 3·5, sank, whilst a black substance floated. The transparent particles scratched ruby, burned to carbon dioxide, and showed octahedral facets.

Among the other products of the electric furnace were: crystallised lime, strontia, baryta, and magnesia; metallic and reguline chromium, manganese, molybdenum, tungsten, uranium, vanadium, zirconium, and titanium; also distilled copper, silver, platinum, gold, tin, iron, and uranium; volatilised carbon and silicon, and many other similar products. The metals were obtained by heating the oxides mixed with powdered sugar-charcoal; and in most cases a carbide of the metal, or a solution of carbide in the metal, was obtained. The presence of carbon monoxide, due to the presence of the carbon electrodes, no doubt contributed to the formation of carbide. In order to obtain the pure metal, therefore, a second operation was necessary, as a rule; the metal was again heated in the furnace in a crucible lined with its own oxide; the combined carbon thus obtained oxygen, and was evolved as oxide, whilst the metal was left in the reguline state.

Moissan made an exhaustive study of the properties of the compact metals, and of their carbides. It would be impossible in a discourse like the present one to do justice to the enormous number of interesting observations which he made; indeed, he added a very large chapter to the book of chemistry. All that can be done is to pick out a few examples to illustrate the character of his work.

Let us first take chromium. This metal was prepared by allowing a mixture of the sesquioxide with carbon to run down a sloping tube of carbon, heated to whiteness in the electric furnace; metallic chromium ran out at the lower end, and Moissan says that it is easy to prepare as much as 20 kilograms of chromium at one operation. The amount of carbon in the product varied between 8·6 and 11·92 per cent. The carbides of this metal were then studied. On melting metallic chromium with a large excess of carbon in the furnace for ten or fifteen minutes, a brittle button was obtained, consisting of crystals of C_2Cr_3. It is unattacked by concentrated hydrochloric acid, by weak or strong nitric acid, or by *aqua regia*, but is acted on slowly by dilute hydrochloric acid. Nor is it attacked by fused potassium hydroxide, although potassium nitrate destroys it easily. Another carbide was produced during the preparation of metallic chromium, covering the surface of the metal with brilliant needles; its formula was CCr_4.

The carbide, produced as the raw material, was converted into the metal by the method already indicated, that is, by fusing it in a crucible lined with chromium oxide, and covering it with the same material. The button of metal thus obtained, however, was "burnt," that is, contained oxide in solution. To remove the oxide, it can be re-melted with lime; or, what is simpler, the original carbide can be deprived of carbon by fusion with lime, the lime forming calcium carbide, together with carbon monoxide. This action is, however, a reversible one; there is a double oxide of chromium and calcium formed, which forms fine crystals. This substance, fused with more carbide, yielded pure chromium. Chromium was found to be unalterable in air, but when heated to 2000° in oxygen it burned, emitting sparks even more brilliantly than iron does. Chromium filings heated with sulphur become incandescent, producing the sulphide. When heated with carbon, CCr_4 is produced. A silicide is produced when chromium and silicon are heated together in the electric furnace, which is very hard, scratching the ruby, and not attacked by acids, or by fused potash or nitre.

This method of refining chromium was applied to commercial "ferro-chrome," and was found to be successful in depriving it of carbon; and it was shown that, starting from chrome-iron ore, ferro-chrome of 60 per cent. chromium could be made by passing it, mixed with carbon, through the electrically heated tube; it contained 6 per cent. of carbon and 1 per cent. of silicon. Potassium or sodium chromate could be made from it by fusion with potassium or sodium nitrate, the iron remaining behind as insoluble oxide. In conclusion, Moissan found that copper, allied with half a per

cent. of chromium, acquired twice the tensile strength of pure copper; it took a fine polish, and was less tarnished on exposure to air than copper.

In a similar manner he treats of manganese, molybdenum, tungsten, uranium, vanadium, zirconium, titanium, silicon (incidentally having discovered "carborundum"); he finds that aluminium is not easily reduced in the furnace, but yields a carbide. In this connexion he in some measure anticipates the "thermite" process, for he projects a mixture of aluminium filings with the oxide of the metal to be produced on to the surface of molten aluminium; in this way he prepared alloys of nickel, molybdenum, tungsten, uranium, and titanium with aluminium.

Moissan also prepared numerous carbides, and submitted them to an exhaustive study. Lithium carbide, prepared from lithium carbonate and carbon in the furnace, has the formula Li_2C_2, and on treatment with water yields pure acetylene.

In our *Proceedings* of the year 1893, Travers described the preparation for the first time of calcium carbide by heating together metallic sodium, calcium chloride, and carbon. A month before, Moissan had stated that the lime of his furnace reacted with the carbon of his electrodes, "forming a carbide of calcium, easy to collect." But it was not until March, 1894, that he described this compound, since become so important industrially. Travers used his carbide for the production of acetylene; but Wilson, who patented the same compound in 1893, in America, was ignorant that the gas evolved on treating it with water was acetylene; indeed, he does not appear to have treated it with water at all. Moissan made a most careful study of this important compound, and described its chemical properties in great detail. He also made the carbides of barium and strontium; and he described the action on them of chlorine, bromine, iodine, sulphur, selenium, and phosphorus; in each case both metal and carbon combine with the element used for the attack.

The action of water on the carbides of cerium, lanthanum, yttrium, and thorium produced in a similar manner is not so simple; acetylene, ethylene, methane, and liquid and solid hydrocarbons were formed from C_2Ce, C_2La, C_2Y, and C_2Th. Aluminium carbide, however, has the formula C_3Al_4, and yields pure methane. Manganese carbide, in its turn, belongs to a different type; its formula is CMn_3; and with water, hydrogen and methane in equal volumes are the products; and uranium carbide, C_3U_2, gives methane and a complex mixture of liquid hydrocarbons.

From these experiments Moissan was induced to propound a theory of the formation of petroleum; he does not consider it exclu-

sive of the production of hydrocarbons by the natural distillation of coal and shale; but he thinks that in certain formations, where the existence of such deposits is improbable, the occurrence of petroleum may be explained by the attack of carbides of the metals by water.

Moissan also prepared many silicides and borides. Among these were silicides of iron, of chromium, and of carbon; although he had obtained crystals of "carborundum" in 1891, he did not at that time publish any account of it; and he concedes the merit of its discovery to Acheson. The borides of iron, nickel, cobalt, calcium, strontium, barium, carbon, and some others were also prepared and carefully studied. These researches took many years, and are a model for accurate experimentation and luminous exposition. They were described in two works, "Le Fluor," published in 1887, and "Le Four Électrique," published ten years later. Since that date Moissan's chief researches dealt with: The preparation of metallic calcium by heating calcium iodide with sodium; its success depends on the easy attack of sodium by alcohol, whilst calcium is hardly affected. The investigation of sodium ammoniums and methyl-ammoniums, obtained by the action of sodium on liquid ammonia and on methylamine; and similar substances obtained from lithium and calcium. The preparation in the pure state of the hydrides of calcium, sodium, and potassium; he showed that these bodies are non-conductors of electricity, and that the hydrogen which they contain must be supposed to exist in combination as a non-metal, in contrast to its condition in palladium hydrogen alloy. In later papers on these compounds, he described a most ingenious formation of sodium formate by the action of carbon dioxide on sodium hydride, and of sodium hyposulphite, $Na_2S_2O_4$, by treating the hydride with sulphur dioxide.

Moissan did not, however, desert his old favourites, fluorine and the products of the electric furnace; for in later years he prepared thionyl fluoride, SOF_2, and sulphuryl fluoride, SO_2F_2, both gases; and he re-determined the density of fluorine in a dry glass vessel. The electric furnace yielded him metallic niobium and tantalum, many metals of the rare earths, and borides of silicon. A silicide of lithium, Li_6Si_2, was prepared; and a new hydride of silicon, Si_2H_6, the analogue of ethane. He also studied the acetylides of metals of the alkalis. His last research, of which an account appeared in the *Compt. rendus* for 1906, p. 675, dealt with the distillation of titanium in the electric furnace. In all, he published more than three hundred memoirs and notices.

This incomplete account of Moissan's work shows how productive his laboratory was; he was full of new ideas, most of them offshoots

of his original great discoveries; much of his work was carried out in conjunction with students, of whom an increasing number came from abroad, for his reputation both as a skilled chemist and as an attractive personality had become world-wide. His work lay almost entirely in the field of inorganic chemistry, and it contributed to turn the tide which had set so long in favour of organic research.

He published, along with many other collaborators, a treatise on inorganic chemistry—"Traité de Chimie Minérale"—in five large volumes, which has a large circulation in France, and in point of detail is a very complete account of inorganic compounds.

Moissan was the recipient of numerous honours, not only in his own country, but also abroad. In 1888, after his isolation of fluorine, he was elected a member of the Académie de Médecine; in 1891, of the Académie des Sciences; in 1895, Membre of the Conseil d'Hygiène de la Seine; and in 1898, of the Comité Consultatif des Arts et Manufactures. He was Foreign Fellow of the Royal Society of London; of our own Society; an honorary member of the Royal Institution, and of the Academies of Denmark, Vienna, Belgium, Upsala, Haarlem, Amsterdam, New York, and Turin, besides numerous others. He was also Commandeur de la Légion d'Honneur.

In 1887 the Institut awarded him the Prix Lacaze, one of its most valuable gifts; he was the Davy medallist in 1896, and the Hofmann medallist in 1903; and he obtained honours from the Franklin Institute of Philadelphia, from the Société d'Encouragement pour l'Industrie Nationale, and the Société Industrielle du Nord de la France; and in 1906, shortly before his death, he was awarded the Nobel Prize for Chemistry.

Moissan was a practised speaker and a perfect expositor. His lectures at the Sorbonne were crowded with enthusiastic students, all eager to catch every word, and he kept their attention for an hour and three-quarters at a time by a clear, lucid exposition, copiously illustrated by well-devised experiments. His command of language was admirable; it was French at its best; the charm of his personality and his evident joy in exposition gave keen pleasure to his auditors. He will live long in the memories of all who were privileged to know him, as a man full of human kindness, of tact, and of true love of the subject which he adorned by his life and work. Perhaps the key to his character lies in his own words: "Nous devons tous placer notre idéal assez haut pour ne pouvoir jamais l'atteindre;" or as our own poet has put it: "O but a man's reach should exceed his grasp; or what's a heaven for?"

S. Cannizzaro in 1858.

From a Portrait by D. Salorson.

To face p. 1680.

CANNIZZARO MEMORIAL LECTURE.

Delivered on June 26th, 1912,
By Sir William A. Tilden, D.Sc., LL.D., F.R.S., Past-President of the Chemical Society.

The minutes of the Ordinary Scientific Meeting of the Chemical Society for June 19th, 1862, contain the following entry: "Messrs. Cannizzaro, Kekulé, Löwig, Malaguti, Marignac, Pasteur, Stas, and Zinin were elected Foreign Members."

Of this illustrious band not one now remains,* and the Society having paid its tribute to each in turn is gathered on this occasion to commemorate the name which, of those enumerated, was the last to disappear from its roll of Honorary Members.

The career of Stanislao Cannizzaro was completed in an age and country full of romance. Born as he was under the reign of a Bourbon in the kingdom of the two Sicilies, he lived to see the miserable conditions which beggared and enslaved his own compatriots swept away; he took a part as soldier and Senator in the regeneration of Italian nationality, and during the latter half of his long life he enjoyed the freedom which belongs to a united people under a constitutional Monarchy.

His experiences as a man of science were no less remarkable, for it may be said he began work almost before modern chemistry, of which he helped to lay the foundations, had been called into existence. When Cannizzaro was twenty years of age, Liebig in Germany, and Dumas in France were at the height of their fame; while in England Williamson's ideas were beginning to attract serious attention. Many years had yet to elapse before a real system could be applied to the masses of facts then so rapidly accumulating.

Stanislao Cannizzaro was born in Palermo on July 13th, 1826.† The family came from Messina, and its members at different times held important offices in that city and elsewhere in Sicily. Stanislao's father, Mariano Cannizzaro, was born in Messina, but he became a magistrate in Palermo and Minister of Police, and later President of the Gran Corte dei Conti. The mother was Anna di Benedetto, a member of a noble Sicilian house. There was a large family, of which Stanislao was the youngest. He was educated

* Kekulé died in 1896, Löwig in 1890, Malaguti in 1878, Marignac in 1894, Pasteur in 1895, Stas in 1891, and Zinin in 1880.

† For the facts relating to his father's life, I am indebted chiefly to Mr. Mariano Cannizzaro

partly at the Reale Collegio Calasanzio, where he won prizes, with distinction especially in mathematics. As may be imagined, the school curriculum in Sicily, as in the whole of Southern Italy, in Cannizzaro's youth was entirely under the control of the priests. Education, "frowned on as a design of the Liberals to revolutionise the State, was so successfully discouraged that in 1837 it was calculated that 2 per cent. of the rural population could read, and not very much more of the dwellers in the towns." * The subjects were confined to the classical languages, grammar, and rhetoric, with a little mathematics.

In 1841, at the age of fifteen, Cannizzaro began the study of medicine at the University of Palermo, and especially the study of physiology under Professor Foderà. The University was at that time in a very imperfect condition, degrees being conferred only in the faculties of medicine, law, and theology. Cannizzaro took no degree, but in 1845 proceeded to Naples, where his sister Angelina had married the Marquis Ruffo, son of King Ferdinand's Prime Minister. Here, after taking part in the proceedings of the physiological section of the scientific congress held in that year, he made the acquaintance of the famous physicist Melloni, and after working for a short time in his laboratory he proceeded, with a warm recommendation from Melloni, to Professor Piria at Pisa. The influence of Piria over his young assistant was fortunately sufficient to determine the latter to devote himself permanently to chemistry. Piria was just then at the height of his fame, justly following his discovery of the constitution of salicin, a very noteworthy feat in those early days of organic chemistry.

Cannizzaro, although an enthusiastic student, could not escape the effects of the political agitation which exercised an influence so powerful on his compatriots at that time. Those were dark days in the history of the country, and the atrocities committed in the name of order by Ferdinand's government had aroused not only the spirit of the Sicilians, but the indignation of, at least, the English people. Beside, Italian soil was occupied in the north by the armies of Austria, there was clerical misrule in the Papal States, and throughout Europe revolution was the order of the day. Cannizzaro responding to the prevalent feelings of patriotic fervour, joined in the premature rebellion in Sicily. Returning from Pisa to his native country in 1847, he joined the Sicilian artillery, and commanded a battery at Messina. After the fall of Messina he was sent to Taormina with a Government commission to oppose the advance of the Neapolitan troops under the General Principe Filangeri, but after March, 1849, the defeat at Novara, and the

* Trevelyan's "Garibaldi and the Defence of the Roman Republic," p. 55.

abdication of Charles Albert, the Sicilians were obliged to retreat towards Palermo, Cannizzaro being among the last to oppose the Neapolitans. On the fall of the Sicilian Government he embarked with some others on board the frigate *Independente*, which, escaping the Neapolitan fleet, succeeded in reaching Marseilles. After some months Cannizzaro made his way to Paris, and having found admission, presumably through the introduction of Piria, into the laboratory of Chevreul, he resumed his chemical studies. Here he joined Cloëz in work on cyanogen chloride and the production of cyanamide, and their results, published in 1851, constituted Cannizzaro's first contribution to the records of chemical research (*Compt. rend.*, 1851, **32**, 62).

At the close of 1851 he was able to return to Italy, having been appointed professor at the National School at Alessandria, where he had the advantage of a small laboratory and the services of an assistant, "un farmacista giovane intelligente" (letter to Bertagnini). Here he was so occupied, body and mind, with his teaching that, as he complained to his friend Bertagnini, he had little hope of being able to pursue his own studies. Notwithstanding these unfavourable conditions, however, he discovered in 1853 the alcohol corresponding to benzoic acid, which he obtained by the action of potassium hydroxide on benzaldehyde (*Annalen*, 1853, **88**, 129), and which he continued to study during several succeeding years (*Ann. Chim. Phys.*, 1855, [iii], **43**, 349; *Nuovo Cim.*, 1855, **2**, 212).

The summer holiday of 1852 was spent with Bertagnini, who had a small private laboratory at Montignoso, and here the friends carried out work on anisic alcohol, which, however, was not published until 1856 (*Ann. Chim. Phys.*, 1856, [iii], **47**, 285). In 1854 Piria, in association with Matteucci, produced the first number of the new journal *Il Nuovo Cimento*, which was to be the organ of the Pisan school, and to the second volume Cannizzaro made the contribution referred to above. *Il Nuovo Cimento* was not established without some suspicion on the part of the Censor, the Chancellor Cardinal Archbishop, that chemistry and physics, "scienze pericolose," might cause some damage to the faith (*Nuova Antologia*, June, 1911, 490).

In 1855 Cannizzaro accepted an invitation to the Chair of Chemistry in the University of Genoa, at the same time Piria* being transferred to Turin, while Bertagnini was appointed to replace him at Pisa.

* That Piria was the founder of the Italian School of Chemistry was attested by Liebig. Piria held Cannizzaro in high esteem, which was repaid by the admiration of the pupil, and expressed many years later in Cannizzaro's "Vita e opere di R. Piria," 1883.

At Genoa there was at first no laboratory, and it was only in the year following his appointment that Cannizzaro could obtain rooms in which to carry on his work.

At this time, or probably earlier, he must have begun to meditate on those fundamental questions in chemical theory which led to the famous "Sunto di un Corso di Filosofia Chimica," communicated, in March, 1858, through Professor di Luca to the *Nuovo Cimento* (**7**, 321). But his philosophical and scientific studies, as well as his teaching, were destined to be once more interrupted by the political events which at this time followed one another so rapidly in Italy. In the spring of 1860, the discontent of Southern Italy, responding to the unhappy events in the North, found vent in the insurrection which broke out in April of that year, although it was crushed almost immediately by the Neapolitan Royalist troops. However, Garibaldi with his famous thousand succeeded in effecting a landing at Marsala, in Sicily, on May 11th, and ultimately forced his way into Palermo. The story has been often told, and is full of the most astounding and romantic incidents.* As soon as Garibaldi had entered Palermo, Cannizzaro started for Sicily with the second expedition under General Medici, although he took no part in any battle. In Palermo he became a member of the Extraordinary Council of State of Sicily.

In October of the following year, 1861, he was called from Genoa to his native town, and was appointed Professor of Chemistry in the University of Palermo. Here, again, he had no laboratory, and it was only in 1863 that provision was made for practical work. His activity extended beyond the duties of the office he held in the University, for beside occupying a position on the Municipal Council he made great efforts to secure the establishment of schools, which were almost entirely wanting, as well as to provide for the higher education of women.† He also established an evening drawing school for workmen, and in this school his only son, then a child, received his first lessons in art. Later he became Rector of the University, and in 1867 he acted as Commissioner of Public Health during one of the severe outbreaks of cholera, in the course of which he lost a sister, struck down by the disease whilst nursing the sick.

Cannizzaro remained in Palermo about ten years, and during this period the work he was able to accomplish in chemical research related chiefly to the derivatives of benzylic alcohol and other aromatic substances. It is interesting to recall in this connection

* See Trevelyan's "Garibaldi and the Thousand."

† *Nuova Antologia* (June, 1911, 492) gives a full account of his benevolent exertions in this and other directions.

the fact that among the young men who came under his influence at that time was one whose name a very few years later became renowned throughout the chemical world on account of the great memoir (1874), in which was established once for all the principle by which the orientation of all the derivatives of the so-called aromatic substances can be determined. Körner's rule is familiar to even junior students of organic chemistry. The names of Körner and Cannizzaro are associated together in the authorship of a paper on anisic alcohol (*Gazzetta*, 1872, **2**, 65).

In 1871 Cannizzaro was called to Rome to occupy in the new University the Chair of Chemistry, which he retained until death summoned him away so many years later. Even in the capital city he again found no laboratory, and he was obliged to suspend his researches whilst occupied in organising the chemical institute which found shelter in the old monastic buildings in the Via Panisperna. Here he ultimately established a school, and in spite of the heavy official duties which devolved on the professor he continued during many years the study of the complex and interesting compound, santonin, and worked out its constitution with the co-operation of his pupils and assistants, Amato, Carnelutti, Gucci, Sestini, Valente, and others.

At the same time that he received the call to the University he was made a Senator of the kingdom, and as a Moderate Liberal played his part in shaping the Constitution, and establishing reform in the affairs of the now united Italy. Among other duties which fell to his lot was the organisation of the Customs laboratory and the State Regia dei Tabacchi. He was also a member of the higher Council of Public Instruction, of which for some time he was President. He further occupied himself with the provision of public instruction in agriculture, and generally in helping forward the advancement of science and of the liberal professions in Italy. When the Congress of Applied Chemistry met in Rome in the year 1906, Cannizzaro was Honorary President, and it was gratifying to the visitors from so many lands to see the vivacity and energy with which the old man, then in his eightieth year, entered into all the proceedings. He was still lecturing, and some of the members had the privilege of hearing him address his class in the lecture room of the Chemical Institute. It was from this room four years later that his remains were borne by a company of his students to their last resting place. We are informed that he continued to lecture until the year before his death: "for him to teach was to live." As soon as he perceived that his strength was failing so much that he could not lecture, all his ailments appeared to increase, and the end soon came. He died on May 10th, 1910.

Cannizzaro married in Florence, in 1856 (or 1857?), an English lady, Henrietta Withers, daughter of the Rev. Edward Withers, who held a living in Berkshire. He left one son, who practices in Rome as an architect, and a daughter.

Active as he was as an investigator in the domain of organic chemistry, Cannizzaro's chief claim to the admiration of his contemporaries and to a distinguished place in the history of modern chemistry is based on the systematic course of theoretical teaching which he sketched in 1858.

To form a just estimate of the influence exercised on the progress of scientific chemistry by Cannizzaro's famous essay, a brief review of the state of knowledge and opinion in the chemical world up to and about the year 1858 is necessary.

The atomic theory of Dalton was just fifty years old, and although well rooted in the literature of chemistry there were not a few who still refused to recognise it, and there were many super-cautious chemists who preferred to speak of it as "at the best but a graceful, ingenious, and in its place useful hypothesis."* Evidence of the persistence of this attitude so late as 1869 is afforded by Williamson's lecture,† and especially by the discussion which ensued upon it. Some thought to perceive a distinction between physical atoms and chemical atoms, but generally they seem to have retained the fundamental notion of Dalton, which conceives each atom to be a sphere existing either alone or in close contiguity with other similar atoms, and separable more or less from one another by the influence of heat. Students at this time were generally unfamiliar with the word "molecule,"‡ for chemists spoke as complacently, and in a sense as justly, about an *atom* of water as about an atom of oxygen. For the most part, also, they had never heard the name of Avogadro. Considerable advances had been made toward the estimation with exactitude of what were then usually, although incorrectly, called "atomic weights," notably by Berzelius, Dumas, Pelouze, de Marignac, and Stas. The figures thus afforded by experiment were only equivalents or combining proportions, uncorrected by reference to any standard, for the excellent reason that there was no standard generally recognised; and even in the use of the term "equivalent" there was the utmost confusion, of which evidence is provided by the statement in one of the most widely circulated text-books of the period (Fownes, 1856) that the

* "Fownes' Chemistry," 6th ed. (1856), p. 210. Edited by Bence Jones and Hofmann.

† *Journ. Chem. Soc.*, 1869, **22**, 328.

‡ The word *molecule* was occasionally used by Dalton, *e.g.*, "Chemical Philosophy," Vol. I., p. 70, and in the sense of atom by Ampère (*Ann. Chim. Phys.*, 1814, **90**, 43).

numbers called equivalents "represent quantities capable of exactly replacing each other in combination," the list of numbers referred to including nitrogen 14, carbon 6, whilst hydrogen was 1, and all were said to be equivalent to oxygen taken as 8. In the same book the law of Gay-Lussac relating to combination of gases by volume is "explained" by the statement (p. 203) that "quantities by weight of the several gases expressed by their equivalents, or, in other words, quantities by weight which combine, occupy, under similar circumstances of pressure and temperature, either equal volumes or volumes bearing a simple proportion to each other." Examples quoted in connexion with this passage show that the volumes of equivalents of elements and compounds as then recognised varied from $\frac{1}{2}$ vol. for O to 2 volumes for HCl and NH_3.

The consequences of bringing them all to the same volume were at this time, and even much later, not considered by the great majority of teachers, and although vapour densities were frequently the subject of experiment, the results were used merely to check the empirical formula deduced from analysis of the substance, and few thought of adopting a standard volume and revising the empirical formula so as to harmonise with it. If, for example, the vapour density of acetone was found, it would be used merely to substantiate the formula deduced from analysis, namely, C_3H_3O (C = 6, O = 8), and "whether the rational formula of acetone is C_3H_3O or $C_6H_6O_2$ or $C_9H_9O_3$, the vapour density does not enable us to decide" (Galloway's "Second Step," 1864, p. 68).

This is surprising in view of the fact that so far back as 1826 Dumas, in the memoir in which he describes his well-known method of taking vapour densities,* refers to the fact that all physicists agree in supposing that in elastic fluids under the same conditions the molecules are placed at equal distances, or in equal numbers in the same volume. The difficulties encountered in the general application of this principle to the determination of formulæ arose chiefly from the lack of trustworthy experimental data. But these were gradually accumulating in the years which followed, and by the time Gerhardt and Laurent began to handle the fundamental propositions relating to theoretical chemistry there was a large body of facts, sufficient as it now appears to have provided safe ground for generalisation.

Up to this time also the conception that the ultimate particles of the elements themselves might contain more than one atom had not been commonly accepted. It was believed that combination could only occur between substances of opposite chemical or electro-

* "Sur quelques points de la Théorie atomistique" (*Ann. Chim. Phys.*, 1826, **33**, 337).

chemical character, hydrogen with oxygen, for instance, but that hydrogen could unite with hydrogen, or oxygen with oxygen, was not generally admitted.

It is evidence of the complete neglect with which Avogadro's great memoir * of 1811 had been treated that chemists generally at this time did not know or had completely forgotten that the constitution of elementary molecules in the gaseous state had been very clearly explained by him. The passage is rather long for quotation in full, but in the second division of the memoir he discusses the case of the "elementary molecules," and his position is indicated clearly enough by the case of water. He says: "Ainsi la molécule intégrante de l'eau, par exemple, sera composée d'une demi-molécule d'oxigène avec une molécule, ou, ce qui est la même chose, deux demi-molécules d'hydrogène." This view of the constitution of elementary molecules did not, therefore, originate with Gerhardt, to whom the idea is usually attributed.

Gerhardt in 1843 had pointed out that the equivalents accepted for organic compounds did not agree with those assigned to mineral substances, and in order that they might correspond with H_2O, CO_2, and NH_3, the formulæ he assigned to water, carbon dioxide, and ammonia respectively, they required to be reduced to one half. At the end of a series of papers on the subject (*Ann. Chim. Phys.*, 1843, **7**, 129, and **8**, 238) he sums up his conclusions in the following sentences:

"Atomes, équivalents et volumes sont synonymes.

"Les densités des gaz sont proportionelles à leurs équivalents."

The fourth volume of his famous "Traité de Chimie Organique" (1856) contains an exposition of his system, in which the molecule of water is taken as the unit, and is represented by the formula H_2O (O=16). From this he was led to represent elementary hydrogen as hydrogen hydride, HH, and gaseous chlorine as chlorine chloride, ClCl. This conception of the constitution of elementary molecules was not derived from any direct consideration of the views of Avogadro or Ampère, whose names are not mentioned. They arose doubtless from acceptance of the principle already acknowledged by Dumas as the prevailing doctrine among physicists, namely, that equal volumes of gases contain the same number of molecules, but Gerhardt never explicitly accepted this principle as a means of settling molecular magnitudes, nor did he seem to give it a position of prime importance among recognised

* Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons (*J. de Physique, etc.*, **73**, 58—76. Paris, July, 1811. Translated in No. 4 Alembic Club Reprints. Also reprinted in full by the R. Academy of Sciences, Turin, 1911.

Al Prof. William A. Tilden
Roma il 13 Aprile 1898
S. Cannizzaro

To face p. 1077.

principles. In his little book * published in 1848 before the issue of his great work on organic chemistry, the following passage occurs (p. 43): "Comme il importe toutefois d'adopter une notation exprimant les plus de faits à la fois, j'ai proposé il y a quelques années, de tenir compte des volumes, et de ramener à un même volume les formules des composés volatils, notamment des composés organiques. . . . Comme OH_2 correspond à 2 volumes j'ecris aussi les corps suivants ainsi: CO, CO_2, NH_3, ClH, NO_2, C_2H_6O, SO_3, etc."

His system of formulæ appears to have been based chiefly on his own view that every chemical change is a form of double decomposition, and he is at great pains to show that in chemical reactions, whether of combination or decomposition, the proportion of water or of carbonic acid involved was never less than the amount represented by the formulæ H_2O and CO_2, in which H = 1, O = 16, and C = 12; and, similarly, the amount of free oxygen or hydrogen was never less than the amount represented by O_2 and H_2 with the values as just stated. In his "Traité" (Vol. IV., p. 568) he distinguished the radical hydrogen from the gas hydrogen, the radical chlorine from free chlorine, and he explains that it is the study of reactions which has led him to write hydrogen gas as made up of the two radicals HH, and chlorine gas as composed of the two radicals ClCl; and he goes on to say: "Dans la nomenclature usuelle le gaz hydrogène serait donc l'hydrure d'hydrogène, et le gaz chlore serait le chlorure de chlore; cela veut dire que le gaz chlore et le gaz hydrogène resultent de doubles décompositions."

This mode of viewing the subject led him into some mistakes, of which an example occurs a few pages further on (p. 571), where he represents the action of hydrochloric acid on zinc by an equation in which the zinc molecule is represented as a double structure like that of hydrogen; thus:

$$ZnZn + ClH = ZnH + ClZn$$

and

$$ZnH + ClH = HH + ClZn.$$

The molecule of mercury is also represented by a corresponding formula, HgHg (p. 575).

As regards the constitution of the molecules of the elements, it should not be forgotten that it was in 1850 that Brodie published his views "on the Condition of Certain Elements at the Moment of Chemical Change" (*Phil. Trans.*, 1850, II, 759, and *Quart. Journ. Chem. Soc.*, 1852, **4**, 194). In this memoir he expresses the opinion "that at the moment of chemical change the same chemical relation exists between the particles of which certain elements consist, as between the particles of compound substances under similar cir-

* Introduction à l'étude de la Chimie par le système unitaire, 848.

cumstances, on which relation the phenomena of combination depend; that, in short (to use the common language), the particles of the elements have a chemical affinity for each other"; and then he goes on to suggest that the term *affinity*, which is unsatisfactory, should be replaced by the term "polar relation," which serves to indicate an analogous condition "between a series of particles undergoing chemical change and a series of particles conducting electricity or magnetism." These views are illustrated by reference, *inter alia*, to the decomposition of oxide of silver by hydrogen peroxide, previously observed by Thénard, and the mutual interaction of cuprous hydride discovered by Wurtz with hydrochloric acid. The former of these two changes results in the evolution of oxygen gas, and the latter in the production of hydrogen gas, and they were explained by Brodie on the assumption of opposite polar relations in the atoms which combined together in pairs

Gerhardt's system of four types—water, hydrochloric acid, ammonia, and hydrogen—was adopted by him only for the purpose of classifying reactions, as he insisted repeatedly that any knowledge of the arrangement of atoms in a compound is inaccessible to experiment. Dumas' earlier theory of types had implied the idea of arrangement in the constituent parts of bodies, and, indeed, the existence of transferable radicals, or residues as they were called by Gerhardt, such as cyanogen, benzoyl, and ammonium, involved some notion of order within the ultimate particle.

At the time under review the conflict between the notation in equivalents and the notation corresponding to Gerhardt's types had not been decided. The notation which presented water as HO and hydrogen sulphide as HS, involved the anomaly that such formulæ represented two volumes of vapour, whilst HCl and NH_3 represented four volumes. The unitary system of formulæ was still unacceptable to the great majority of chemists, although many occupied themselves in testing the capacities of the several systems of types with a view to the discovery of relationships among the very numerous carbon compounds daily issuing from every laboratory. The water type of Williamson, the ammonia type of Wurtz and Hofmann, the hydrochloric acid and hydrogen types of Gerhardt afforded for some years a basis for discussion which, although ultimately fertile, inasmuch as it led indirectly to the idea of the linking of atoms, was too often barren enough for all immediate practical purposes. The time had not arrived when the property of atoms, which is now called valency, could be recognised, and although Frankland as early as 1852 (*Phil. Trans.*, 1852, **142**, 417) had drawn attention to the fact that the combining powers

of elements are limited and constant, it remained until many years later among the numerous unutilised curiosities of observation. It might be said that those who made use of the water type and the ammonia type for various compounds implicitly admitted the idea that the oxygen and the nitrogen in these compounds respectively did hold together, in the one case two and in the other case three atoms. This, however, was not definitely recognised until much later, when, in 1858, Kekulé (*Annalen*, 1858, **106**, 129) and Couper (*Ann. Chim. Phys.*, 1858, **53**, 469; *Phil. Mag.*, 1858, [iv], **16**, 104) independently showed that in carbon compounds the element carbon must be the nucleus to which the other atoms are attached, and that atoms of carbon, in such compounds, must be united to one another.

At this point it would be, to say the least, unjust not to call to remembrance the great services to science rendered throughout this period by one who was then the junior secretary and is now the senior Fellow of the Chemical Society. If the expositions* addressed by Odling to the Society, and thence to the chemical world outside, failed to clear away much of the confusion and many of the anomalies then permeating theoretical chemistry, it was due to no lack of clearness of thought, knowledge of facts, or cogency of reasoning on the part of the lecturer, but rather to the conservative indisposition to change which often enchains the scientific world, in spite of the precepts of the science which it professes.

During all this long period the name of Avogadro had been treated with a neglect which is scarcely compensated by the recognition now accorded to it nearly a century after his time. Among the French, Ampère gets more credit in this connexion than seems to belong to him, for his paper (*Ann. Chim. Phys.*, 1814, **90**, 43) three years later than the memoir of Avogadro shows little evidence that he attached the same importance to the theorem that equal volumes of different gases under the same conditions contain the same number of particles as did Avogadro. The memoir of Ampère is chiefly devoted to a consideration of the probable forms of the "particules" (molecules) of crystallised substances.

Even those chemists who are generally supposed to have made use of Avogadro's idea have neglected all reference to its origin. Gerhardt, for example, ignored the Italian physicist, and Dumas in the paper on vapour densities already quoted only mentions his name in the following passage, which forms the conclusion of the memoir: "Nous sommes bien éloignés encore de l'époque où la

* Especially "On the Atomic Weights of Oxygen and Water" (*Quart. Journ. Chem. Soc.*, 1858, **11**, 107).

chimie moléculaire pourra se diriger par des règles certaines, malgré les avantages immenses que cette partie de la philosophie naturelle a retirés des travaux de MM. Gay-Lussac, Berzelius, Dulong et Petit, Mitscherlich, ainsi des vues théoriques de MM. Ampère et Avogadro. L'activité singulière de M. Berzelius et le bon esprit des chimistes dont il a enrichi l'Allemagne pourraient cependant faire espérer sur ce sujet important une révolution prochaine et durable."

It was not, however, until thirty years later that this revolution was brought about, and its author was a chemist from no northern school. The year 1858 must for ever be distinguished in the history of chemistry, for it was then that Cannizzaro led the way out of the darkness in which all had been so long struggling.

After this preamble we may more easily realise the nature and extent of the revelation, as it may well be called, which students of chemistry owe to Cannizzaro. That it remained for some years almost unknown may be attributed in part to the barrier constituted by the language in which his essay was originally published. But it is not creditable to the chemists of 1860 that the Congress held at Carlsruhe in September of that year, at which Cannizzaro was present and expounded his views, should have dispersed without a general acceptance of the fundamental principles which to us seem unassailable. The only excuse which presents itself now is the fact that at this period the difficulties arising out of dissociation of compounds like sal-ammoniac and sulphuric acid when volatilised by heat, and which gave rise to the so-called anomalous vapour densities, had not been cleared away. To contend, as some speakers seem to have done, that these subjects are matters of opinion, and that every scientific man is entitled to perfect freedom in respect to the views he adopts, is to misunderstand the case. In art, in which field sentiment, emotion, and taste are the only considerations involved, complete freedom is clearly necessary, but in science whenever facts have been established and an agreement has been arrived at in regard to fundamental assumptions, reason ought to be the only, as it is the sufficient, guide. Unfortunately, this has not always been the case.

It is only fair to mention that of those chemists who were present at the Carlsruhe Congress in 1860, one at least came away convinced. In a prefatory note to the German edition (published in 1891) of Cannizzaro's "Sketch," Professor Lothar Meyer relates how he received at the meeting a copy of this paper, which he read with surprise at the clearness with which all the most important difficulties were removed. He says: "It was as though scales fell from my eyes, doubt vanished, and was replaced by a feeling

of peaceful certainty." In 1864 Meyer published his well-known treatise on the "Modern Theories of Chemistry," in which the views of Cannizzaro are fully developed.

To those who have read Cannizzaro's "Sketch of a Course of Chemical Philosophy," of which a belated English translation has been produced by the Alembic Club, it must be a matter of wonder that the facts and arguments set forth should not have been sufficient to have cleared away the previous confusion immediately. With small and unimportant corrections, it represents a course of instruction which might have been given as embodying the accepted views of the chemical world down to quite recent times, and a perusal of this essay, even now, would be of the utmost value to many teachers.

Cannizzaro's "Sketch" begins with the following words*: "I believe that the progress of science made in these last years has confirmed the hypothesis of Avogadro, of Ampère, and of Dumas on the similar constitution of substances in the gaseous state; that is, that equal volumes of these substances, whether simple or compound, contain an equal number of molecules; not, however, an equal number of atoms, since the molecules of the different substances, or those of the same substance in its different states, may contain a different number of atoms, whether of the same or of diverse nature."

The author then proceeds to trace the history of this conception, of the consequences to chemical theory, and of the ideas which prevented the immediate acceptance of this hypothesis, and the confusion which resulted from the failure to distinguish molecules from atoms. In order to bring harmony into the various branches of chemistry, he then shows that by applying the hypothesis of Avogadro the weights of molecules may be determined before their composition is known, and that a knowledge of their composition is not necessary to this end. Having settled the molecular weights of a series of substances containing one element in common, the discovery is made that the different quantities of the same element contained in different molecules are always whole multiples of one and the same quantity, which represents the atomic weight. After studying the constitution of various volatile chlorides, bromides, and iodides, the question of the constitution of mercuric and mercurous compounds arises, and the author proceeds to show that the smallest proportion of mercury present in any molecule containing that element is 200, and that this is therefore the atomic weight of the metal. This number is then confirmed by appeal to the law of specific heats. The analogy of the chlorides

* I have made use of the *Alembic Club* version in these quotations.

of copper with those of mercury next leads to the examination of these compounds, but as the vapour densities of these salts are not known, the specific heat of copper and of its compounds leads to the number 63 as the atomic weight of copper. Whether this is the molecular weight of the uncombined metal there is no means of knowing until the vapour density of this substance can be determined. Many other metals are then examined, and the author points out that in such cases as tin, which produces compounds volatile without decomposition, and of which the molecular weight can be determined, the atomic weight deduced from specific heat is in agreement with that deduced from vapour density. But then the question arises: "Are the atoms of all these metals equal to their molecules, or to a simple submultiple of them?" And he proceeds. "I gave you above the reasons which make me think it probable that the molecules of these metals are similar to that of mercury; but I warn you now that I do not believe my reasons to be of such value as to lead to that certainty which their vapour densities would give if we only knew them." Herein he differs from Gerhardt, who had represented the atoms of all the metals as fractions of the respective molecules, as in the case of hydrogen.

A little later Cannizzaro comes very near to the modern idea of valency when discussing the capacity of saturation of different atoms. When referring to diatomic radicals as "those which, not being divisible, are equivalent to two of hydrogen or to two of chlorine," he proceeds to show "that cacodyle, C_2H_6As, methyl, CH_3, ethyl, C_2H_5, and the other homologous and isologous radicals are like the atom of hydrogen, monatomic, and, like it, cannot form a molecule alone, but must associate themselves with another monatomic radical, simple or compound, whether of the same or of a different kind, and that ethylene, C_2H_4, propylene, C_3H_6, are diatomic radicals analogous to the radicals of mercuric and cupric salts, and to those of the salts of zinc, lead, calcium, magnesium, etc.; and that these radicals, like the atom of mercury, can form a molecule by themselves. The analogy between the mercuric salts and those of ethylene and propylene has not been noted, so far as I know, by any other chemist."

There is much more in the "Sketch" which was important for the elucidation of the views put forward by the author, but the extracts given are sufficient to show how clear, how systematic, and how logical was the mind which could thus choose out from the tangled mass of fact and fiction constituting chemical theory in his day, the materials for a consistent, orderly, and productive system of scientific chemistry.

What Cannizzaro did for chemistry may be broadly stated under the two following heads:

First, he laid down for all time the two principal methods by which atomic weights are determined, the one by reference to the molecular weights derived from an application of Avogadro's rule, and the other by the adoption of the principle originally discovered by Dulong and Petit as to the general relation of atomic weight to specific heat among the solid elements, and he showed that these two methods when applicable to the same case lead to the same results.

Secondly, he placed inorganic chemistry in a new light by applying to inorganic compounds the same principles which had been applied to organic compounds, and thus finally disposed of the superstition which had hovered so long in the minds of chemists that organic chemistry was subject to laws different from those prevailing among mineral substances.

There is, in fact, but one science of chemistry and one set of atomic weights.

It will not be without interest to recall some of the consequences of the ultimate adoption, tardy as it was, of the principles laid down by Cannizzaro. The unanimity which has prevailed among chemists during the last forty years or more as to the fundamental principles inculcated by Cannizzaro is a proof that his system is not only reasonable but is practically convenient. We are not now divided into parties on the subject of atomic weights, and although some may still incline to use hydrogen as the unit, whilst others prefer an exact integer for oxygen, these differences do not affect the notation nor the common language of chemistry. As a result of a uniform standard for atomic weights we now possess a natural system of classification of the known elements in the form of the periodic scheme with all its consequences, which I need not describe to a Society of chemists. Out of the revised and uniform system of atomic weights we also have a universally acknowledged system of constitutional formulæ, based on valency, which we may define as the habit in regard to combination exhibited by the several elementary atoms, without necessarily forming any hypothesis as to the cause or nature of chemical "affinity." The wonderful discoveries which have been brought to light in the department of stereochemistry provide a body of evidence in favour of atomic structure which can never be set aside; and the day is now gone by when serious support can be found for any form of anti-atomic doctrine, since we have been shown how single atoms can be seen and counted.

That all this knowledge would have come into the possession of

mankind sooner or later cannot be doubted, but that this generation enjoys all the fruits of experiment in chemistry we owe to Cannizzaro. Without the clear light which his doctrine cast into the dark places of chemical theory sixty years ago chemistry might have remained a mass of unclassified, incoherent, and perplexing facts.

This is why it is incumbent on this generation of chemists to do honour to his memory. The Chemical Society cannot be charged with indifference to the great services rendered to science by Cannizzaro, for, as mentioned at the outset, his name was placed on the limited roll of Honorary Members of the Society so far back as 1862. Ten years later he was invited to give the second Faraday Lecture, and again in 1896, on the occasion of his seventieth birthday, an address was presented to him on behalf of the Society, in which full expression was given to the feelings of respect and admiration entertained by all the Fellows toward the veteran chemist.

The Royal Society, also, awarded to him in 1891 the Copley Medal, which is regarded as the highest honour in the power of the Society to bestow.

Although English chemists have thus given what may be called official recognition to the author of the great reform, it would be unbecoming in any of us to hint at indifference or injustice on the part of French or German chemical writers while there are large and prominent English treatises in which the name of Cannizzaro is not even mentioned. Surely this is an occasion when in remembrance of the unity of scientific thought throughout the world, fed by the contributions of all nations, a plea may be entered, not only for justice to individuals, but for complete international impartiality in matters of science.

Italian science is no mushroom growth. Before our own Royal Society was founded, or perhaps even thought of, before the French Academy of Sciences came into existence, Galileo and Torricelli were making discoveries of world-shaking significance. In those times, however, to have observed natural phenomena, and even to be suspected of holding unfamiliar, novel, and therefore heretical opinions about the world in which man is placed, was to draw down on the unhappy philosopher the condemnation of political and ecclesiastical ignorance and fanaticism. No wonder that those whose interest was excited by the new knowledge then coming to light endeavoured to conceal their discussions and places of meeting under all kinds of fantastic and often ridiculous masquerade.*

* See, for example, Disraeli's *Curiosities of Literature*: "On the Ridiculous Titles assumed by the Italian Academies."

Happily such prejudice, although occasionally showing itself, as in the instance already mentioned of the publication of *Il Nuovo Cimento*, is now powerless, and the neglect of Avogadro's hypothesis cannot be put down to the influence of ecclesiastical authority. The obscurity which prevented its recognition arose out of the very nature of chemistry itself, and even the prosecution of research seemed for a time only to add to the prevailing confusion by producing crowds of new and unclassified facts. Science had, in fact, to wander in the wilderness until the great leader came to show the way. That Avogadro's life should have come to a close only two years before the formal proclamation and application of his doctrine before a congress of chemists seems a harsh dispensation, but if he had lived only a little longer it would surely have been to him an added satisfaction that that doctrine should have been established by his fellow-countryman.

As to Cannizzaro himself, we may rejoice that he not only led chemistry out of the shadow of the pillar of cloud, but in living to see the complete triumph of the system he had laid down so long ago he truly entered into the enjoyment of the promised land.

On the scutcheon which bears the names of Galileo and Torricelli, of Galvani and Volta, of Avogadro and Piria, Italy may proudly write another glorious name, Stanislao Cannizzaro.

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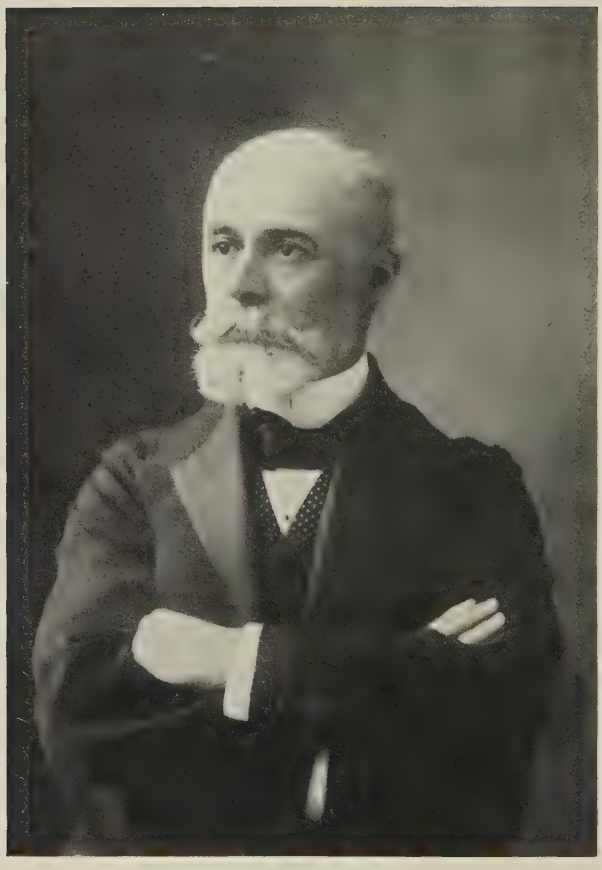

BECQUEREL MEMORIAL LECTURE.

DELIVERED ON OCTOBER 17TH, 1912.

By SIR OLIVER LODGE, D.Sc., LL.D., F.R.S.

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The Discovery of Radioactivity, and its Influence on the Course of Physical Science.

Part I.—General.

The atmosphere of physical science at the present time is rather a strange one. It is characterised by a large amount of speculative activity, on the one hand, and by an exceptional amount of fundamental scepticism on the other. The two attitudes in fact coexist, may coexist in the same individual, and one may be a consequence of the other. For much of the speculation is sceptical in origin, and much of the scepticism is speculative.

There was a time, within easy memory, when the progress of discovery was placid and peaceful. It seemed to proceed along well-worn channels, and to be based upon the most thoroughly substantial knowledge of the past. The great Victorian era in physics was a development of Newtonian mechanics; and the foundation-stones of science seemed well and truly laid.

Philosophers and biologists attended to their own fields of work, and so for the most part did mathematicians and chemists; each group proceeding on its own lines without much regard for the others. Now, all is changed:—

Chemistry has borrowed the idea of evolution from biology, and is trying to extend it from the origin of species to the origin of atoms; though some chemists reject all this as baseless speculation, and pour modulated scorn upon the few recent discoveries which physicists are willing to accept.

Biologists have been ultra-speculative in their quest for the origin of life, and are turning their attention to metaphysics and philosophy, some of them in an energetic and pugnacious manner.

Mathematicians disport themselves destructively among what have seemed the realities, the very data, of physics; distributing an atmosphere of doubt and hesitation almost equally over space, time, matter, and motion, and treating the ether with a veiled contempt. Philosophers question the correctness of our most fundamental laws—doubting, for instance, even the conservation of energy, and readily assimilating the sceptical utterances of those whom I have for the nonce described as mathematicians, though it is but an active group or school of mathematicians who take this line.

And physicists, or some of them, are seeking to dispense with Newton's laws of motion, to supersede that dynamical basis on which they have built for so long, to regard all laws as merely

conveniences of expression, and are trying if they can manage to sustain their science on a basis of action at a distance, fluid electricity, corpuscular light, and caloric heat.

General Effect of New Discoveries.

Bethinking oneself of a cause for all this, it appears that, whenever a discovery of striking novelty has been made, there is a tendency to consider that it not only supplements, but also supersedes and even negatives, a great many of the opinions which were held before; and hence an epoch of discovery is often followed by an era of scepticism.

Discoveries are of two chief kinds—the discovery of law and the discovery of fact. The two tend to become inextricably interwoven: the discovery of law often leads to the discovery of new facts, and the discovery of new facts to either the formulation of new laws or new modes of statement, or to the resuscitation of discarded ones.

As examples of the discovery of *law*, I instance Newton's gravitational theory of astronomy, and Maxwell's electromagnetic theory of light. Discoveries of this kind take their place among the most prodigious efforts of the human intellect.

Smaller in achievement, but great as generalisations, I naturally mention also the atomic theory of chemistry and the conservation of energy.

As examples of the discovery of *fact*, I might instance the prehistoric discovery of flame, the discovery of static electrification, of the electric current, and of magneto-electricity; and with these I would place the discovery of the electron, and the discovery of spontaneous radioactivity.

Of all the facts discovered during the last half century, I suppose that Röntgen's *X*-rays excited the most popular astonishment; and certainly they were sufficiently new. Nevertheless, existing theory had a place for them, as soon as the electronic notion of cathode rays was admitted—at least, on the assumption that they are pulses in the ether, a view held by most people, and still to be regarded as orthodox. For their immunity from refraction was provided for in Helmholtz's singularly comprehensive "Theory of Dispersion," their penetrative quality was a natural consequence of the thinness of the pulse shell; whilst their origin, as due to the sudden stoppage of a minute electric charge, was not only accounted for, but actually necessitated, by the radiation theory of Larmor.

Hence, if called upon to compare the discovery of Röntgen with the discovery of Becquerel, I should give the palm of novelty to the latter; for the spontaneous splitting up of atoms, and the conse-

quent expulsion of constituent fragments, was not provided for on any theory. It was a revolutionary new fact; although it is true that this view of it was not immediately recognised as an explanation, and although certainly Larmor's electronic theory of radiation, combined with Zeeman's experimental discovery, made some of us very willing to recognise the truth of the disintegration hypothesis as soon as it was promulgated on a basis of fact. Meanwhile, and quite independently of any explanation, the bare fact of radioactivity, with a convenient means of detecting and measuring it, was quickly followed by the brilliant and exciting discovery by Madame Curie of a substance which exhibited the power to an extraordinary degree.

A discovery of real and essential novelty can never be made by following up a train of prediction. It is often made during the process of following a clue, but the clue does not logically lead to it. A really new fact comes always as a side-issue—something unexpected and something that might easily have been overlooked. In so far as it fails to have these characteristics, it cannot be essentially, and in the completest sense, new. The discovery which has been pointed to by theory is always one of profound interest and importance, but it is usually the close and crown of a long and fruitful period; whereas the discovery which comes as a puzzle and a surprise usually marks a fresh epoch and opens a new chapter in science.

Discovery of Radioactivity.

So it is with the discovery of spontaneous radioactivity. The thing that was being looked for by Monsieur Henri Becquerel was the possible emission of Röntgen rays by a substance in a state of fluorescence. It was a reasonable thing to look for, although no theory exactly pointed in this direction; and had it been found it would have been an interesting extension of our knowledge; but the kind of radiation actually detected turned out, when critically examined, to be for the most part not Röntgen rays at all, but corpuscular, and to have nothing to do with fluorescence.

Stimulated by his father's researches in the fluorescence of minerals, and by the possession of many fine specimens, among others a beautifully fluorescent salt—the double sulphate of uranium and potassium—which had been made by him for his father many years ago, Henri Becquerel set himself carefully and critically to examine the kind of penetrating radiation which fluorescent substances exposed to light might possibly be found to emit, such as was also in a preliminary way detected by Niewenglowski, and later confirmed by Troost. What he sought he did not find, but by

deserved good fortune he had the happiness to find something much more important, thus writing his name large in the history of Chemistry and Physics for all time.

The process of discovery is well known, but may be briefly recapitulated. This will, however, be most conveniently done later on, when giving a general outline of his life work.

Such a discovery is quite easy to miss. The late F. Jervis Smith, of Oxford, told me that he missed the discovery of Röntgen rays by a trifle; and other experimenters with Crookes's tubes must have missed it too; for whenever the vacuum in such a tube rises considerably, *X*-rays are likely to be emitted, and to take effect, whether perceived or not, on anything susceptible in their neighbourhood. Jervis Smith, in fact, noticed that boxes of photographic plates which he needed for his work were liable to be fogged if allowed to remain in the neighbourhood of active Crookes's tubes. Presumably he thought the cause to be some merely chemical effluvium, such as ozone or oxides of nitrogen getting into the box, or perhaps he did not speculate on the cause at all, but merely regarded it as a nuisance, interfering with the steady course of his work. Anyhow, he seems to have instructed the laboratory attendant to keep the boxes in a cupboard well away from the fogging influence—a most natural thing to do, and one with which every experimenter must sympathise.

Röntgen, however, as is well known, instead of a box of photographic plates, happened to have a surface coated with fluorescent salt near his vacuum tubes, and although screened from the light its shine caught his eye in a more attractive and attention-compelling manner.

In Becquerel's case the phenomenon looked for appeared to exist, in the way expected, although it was feeble and needed long exposure; but repetition in different circumstances showed that the agent which was expected to produce the effect, namely, fluorescence under the action of light, was inoperative: the action turned out to be spontaneous, and to be dependent only on the kind of mineral used. So much so that no method of hastening or stimulating—nor, indeed, of retarding—this kind of radioactivity, beyond judicious selection of substance, is known to this day.

The following statement concerning the discovery is made by Professor the Hon. R. J. Strutt:

"It occurred to Professor Henri Becquerel, of Paris, to try whether these salts, when luminescent under the influence of light, would give out Röntgen rays. He exposed a photographic plate, wrapped in black paper, to the action of the luminescent salts, and found, after an exposure of some days, that a distinct impression had been produced on the plate,

which appeared on development. It was natural to conclude that Röntgen rays were given off, as had been thought likely.

"Extraordinary as it may seem in face of the result, this conclusion, as well as the reasoning which led to it, was quite mistaken. We now know that the fluorescence of the glass has nothing to do with the production of Röntgen rays. We know, further, that the fluorescence of uranium salts is quite unconnected with the invisible rays which they emit. And lastly, we know that these latter are of a quite different nature from the Röntgen rays! It seems an extraordinary coincidence that so wonderful a discovery should result from the following up of a series of false clues. For we can obtain the Röntgen rays even better by letting the cathode rays fall on a metal surface which is not fluorescent instead of a glass one which is. We can obtain invisible radiation, able to penetrate opaque substances, from uranium in the metallic form, which is not fluorescent. And lastly, as we shall see in the sequel, these uranium rays differ altogether in their nature from the Röntgen rays."

All this does not detract from the merit of the discovery; it rather enhances its practical importance, for, as we have already said, it is a feature inevitable when the facts to be discovered are really and essentially new.

Rapid Survey of Immediate Developments.

Discovery of the nearly non-deflectable and readily absorbable, or α, rays was made by Professor Curie by the electrical method. The most important examination of their properties was made by Professor Rutherford. His results were confirmed by M. Becquerel, who likewise examined the α-rays emitted by polonium, where they are unaccompanied by rays of the β- and γ-varieties, and showed that their magnetic deviation increased at a distance from the source.

An early photographic study of β-rays, and of their magnetic deflexion, was made with fair completeness by Becquerel himself. One of his experiments, exhibiting the deflexion in a striking way, consists in placing a little radium salt in a lead vessel on the back of a photographic plate—which is thus screened from any direct action—and then deflecting the rays, by means of a magnet, right round on to the under surface of the plate, whereon shadows of interposed objects can be thrown in curious fashion by these circularly-travelling rays.

The non-deflectable but very penetrating variety, the so-called γ-rays, were discovered by Villard, whose results were soon confirmed by Becquerel.

The discovery of the new element radium followed on a purely quantitative investigation as to the radioactivity of different materials carried out with exemplary pertinacity and genius by Madame Curie; just as the other rather sensational and admirable

discovery of argon resulted from a quantitative investigation by Lord Rayleigh into the varieties of nitrogen apparently obtainable from different sources.

In both these cases the discoverer himself, with a colleague, worked out many of the properties of the new material; in the case of Becquerel this work was from the first conspicuously shared in by others; thus, Sir William Crookes chemically separated off the greater part of the activity of uranium, as what he called uranium-X, and by systematic treatment, renewed after the lapse of a year, detected the prime facts of (a) the gradual decay in its activity, and (b) the renewal of the activity of the original stock to a compensating extent: thus beginning to open the eyes of physicists to what was really happening, and paving the way for the brilliant and extensive series of experiments by Professor Rutherford and his associates.

The history of all this is so recent, the facts are so numerous and so fairly well known, they are related in so many accessible books, and they are of so great bulk and variety, that it would be impossible usefully now even to touch upon them or to attempt to follow the historical course of development any further. Suffice it to say that Rutherford measured the atomic weight of the α-particles by applying a magnetic field to their trajectory, and thereby showed that they were corpuscular, not in the electronic sense but in a sense definitely material, being probably either a molecule of hydrogen carrying the electrolytic unit of positive charge, or else an atom of helium with a double unit of charge; and he also displayed a gas-like emanation of high atomic weight, great activity, and short life; on the strength of all of which he, together with Soddy, started the idea of atomic disintegration, not as a speculation, but as an actually observed fact. Later Ramsay and Soddy by spectrum analysis definitely established helium as one of the products of disintegration of this radium emanation, which itself appears to have a characteristic spectrum and is regarded as a short-lived element.

In addition to the atomic bombardment or α-particle projection, electrons are thrown off as if from a cathode, although with exceptional velocity, as β-rays; and γ-rays are likewise ejected, apparently akin to those of Röntgen, although with exceptional penetrating power. All these exert an ionising action on the substances through which they travel, into the consequences of which a great many observations have been made by Professors Barkla, Townsend, and others; and there appear to be other rays, probably electrons travelling at too slow a rate to ionise effectively and perhaps associated with emission of α-particles, which have been called δ-rays.

But their slowness is relative, for it is about 3×10^8 c.g.s. or 2000 miles a second.

All these forms of activity are of profound interest, but their importance is overshadowed by the less purely physical, and more directly chemical, phenomena—namely, the emanation, the α-rays, and the other products of disintegration; for thus is demonstrated, for the first time in the history of science, the conversion of one substance into another, the gradual breaking up of an atom by some kind of successive explosions or disruptions, and the consequent generation of one substance after another; among which radium and its emanation, and possibly lead, occur successively at the heavy or gun end, whilst helium and probably hydrogen are found at the light or shot end of the explosion.

(Taking this as the origin of all the lead there is—that is, assuming that it has all descended either from uranium or from some heavy atomed substance of which uranium is the best known surviving representative and a stage through which the process must have passed—radium being another stage, but too short-lived to be usefully considered in the present connexion—a little arithmetical calculation concerning the age of the earth, in this sense, can be made, thus:

Let U_0 represent the original amount of uranium at the beginning; and let it decay at rate k, so that after a time, t, the residue in existence is

$$U = U_0 e^{-kt}.$$

Let lead represent the final result of the decay, itself being considered comparatively permanent, so that the amount of lead now existing is

$$Pb = U_0 - U.$$

Finally, let the amount of lead existing at the present time be n times the amount of uranium now existing, so that

$$Pb = nU;$$

it will follow, by combining these three equations, that the time elapsed since the beginning of the planet in this sense is

$$t = \frac{1}{k} \log_e (n + 1).$$

Now Professor Rutherford's estimate of the numerical value of the logarithmic decrement of uranium is 10^{-9} per annum; hence $1/k$ equals a thousand million years.

What estimate to make for n, the ratio of the extant lead to the extant uranium at the present time, I have no idea; but the datum only enters into the result under a logarithm, and therefore does not affect its magnitude very conspicuously. If we guess, from the relative prices, that $n = 20$, the calculated age is 3000 million years;

whilst if we make a much larger estimate and suppose n to be 200, the 3000 only increases to 5000; and, inversely, if n is only 2, the age is still 700 million years.)

It is needless to emphasise the extraordinary suggestiveness which the instability and intense energy of atomic structure, thus demonstrated, confers upon our ideas of material atoms in general, since it is surely probable that the stability of the atom of the better known elements, especially of the heavy ones like lead, mercury, and gold, is, after all, only a question of degree. Some substances last a few minutes, others a few weeks or years, some centuries, and others millions of æons—these last being naturally more plentiful, like a population with a low death-rate—yet it must surely be considered unlikely that any such atomic groupings are so devoid of internal energy as to be endowed with an absolutely permanent structure incapable of further subdivision.

(Incidentally, I would heartily deprecate any squeamishness about applying the historic term "atom" to elementary units, able to give a definite spectrum and to form chemical compounds of customary character, merely because the progress of discovery has rendered the derivation of the word inappropriate.)

Intrusion of Scepticism.

So far, it has all seemed plain sailing; but now has come the era of scepticism, and an attempt to limit science to purely material entities and to reduce Physics to a sort of glorified Chemistry, to return, in fact, to the kind of ideas which prevailed in the golden age of Chemistry, near the early part of last century, and to discard everything relating to an ether of space.

For instance, as to the nature of the γ-rays, Professor Bragg, late of Adelaide, now of Leeds, has raised an interesting controversy; and has adduced experiments of his own in support of his view that they, as also their congeners the X-rays, are not ether pulses at all, but are corpuscular; being neutral molecules, consisting, it may be, of positive and negative electricity in combination, ejected in a singularly penetrating manner; ejected possibly, not with exceptionally high velocity, but with their electric field so shut up in the molecular interior as to have no links with the outside world, and therefore to be able to travel far through crowds of other molecules without ionising them, and so without being stopped by the exhaustion of energy required for the ionising process. So long as the oppositely charged hypothetical constituents are combined, they have little chemical influence; but Professor Bragg supposes γ-rays to be broken up after a certain length of adventurous journey, and thus, by dissociation, to give rise to

β-rays, and I suppose to some kind of positive rays also. Certainly γ-rays, as they are absorbed, do give rise to β-rays; but this is also a natural consequence of their nature on the orthodox or ether-pulse theory; for just as pulses are generated by means of suddenly stopped electrons, so, in the act of starting other electrons, the pulses may be destroyed.

Professor Bragg's arguments as to their corpuscular nature are based on the secondary effects of γ-radiation, and on the unsymmetrical character of the resulting β-ray distribution before and behind a pair of absorbing plates of different obstructive powers. The arguments are set forth in a properly substantiated manner by their author, and are not to be treated cavalierly. They appear to have secured the adhesion of Professor Callendar, who, in his Presidential Address to Section A at Dundee this year, expressed approbation of Professor Bragg's view; but for myself I feel unable to entertain the idea seriously, not only because, so far as I can follow the argument, it appears far from crucial, but because the ether pulses of the orthodox view are so clearly indicated and indeed necessitated by theory. This is markedly true in the case of X-rays, which are known to arise at the sudden stopping place of rapidly flying electrons; and X-rays are not supposed by anyone to differ greatly from γ-rays.

Larmor's radiation-theory makes the rate of loss of energy of any accelerated electric charge e quite definite, and equal to $\frac{2\mu e^2}{3v}(\text{acc})^2$, where v is the velocity of light.

This furnishes in my judgment a quite fundamental point of view. Ethereal radiation is certainly due to the acceleration of electrons—proportional, in fact, to the square of the acceleration. So when an electron is suddenly stopped or started, an ether pulse is inevitable. In the case of stoppage we call the pulse an X-ray; in the case of starting we call it a γ-ray. And the properties of the thin shell of radiation, which *must* then be started, agree with the known properties of X- and γ-rays, which all admit to be alike.

This statement Professor Bragg and those who adopt his opinion will somewhere disagree with, for reasons given; although in what way precisely they meet the theoretical objection, manifestly—or at least superficially—opposed to the conclusion which they draw from the experiments, I do not yet know, although I can make a surmise from some considerations which follow.

Certainly quickly-flying electrons are stopped at the target of a cathode-ray tube; and certainly electrons are started, with still higher velocity, and more suddenly, at a source of radioactivity of the kind which emits electrons—such as radium-C. When only

α-rays are emitted, γ-rays are not found, or are not plentiful; but they invariably accompany β-radiation; and the reason for this is manifest in the light of an ether theory of radiation.

The question therefore arises as to what ethereal radiation is really like. In so far as Professor Callendar intends to advocate a dual constitution for the whole ether of space, making it consist essentially of interlocked positive and negative electricity—which whatever it really means must at least denote two constituents of exactly opposite properties which are constantly being sheared, that is, strained in opposite directions (compare "Modern Views of Electricity")—I am in sympathy with the attempt, for I have long felt that the progress of discovery would lead us somewhere in that direction, although a great deal more definiteness must be introduced before it is anything but a guess and an anticipation. On this view, however, it becomes just possible to conceive of an isolated unit of ether travelling among the rest, like a minute ejected double corpuscle, a combined plus and minus unit of charge, of the order of electronic size without associated matter; not so much an ether pulse as a minute ether projectile. The idea is not unreasonable, but at present I am unable to agree, without further evidence, that it represents the probable nature of γ- and X-rays.

There are those, however, who hold that even light, which for a century has certainly seemed to consist of ethereal waves or pulses, is likewise corpuscular; and that if it is not wholly explicable in terms of particles shot off from bodies, such ejected particles must form the beginning and substratum of an explanation, with something periodic superposed upon the projectiles, after the manner of Newton.

It is not surprising that an attempt should be made to revive in some form the corpuscular theory of light, even if light be now regarded as an electric manifestation; for electricity, too, has become corpuscular, and the flow of electricity through metals is now regarded as a streaming of actual bodies—detached, or so nearly detached as to be readily interchangeable, from the fixed atoms of a solid, and therefore migratory—flowing from one metal to another across a junction as a fundamental kind of material thing which is able to exist in association with every kind of matter. Its association is loose enough in metals, which are therefore good conductors; whereas in another class of substances the corpuscles are so tightly held in combination with individual atoms that they cease to be migratory, and the substance is an insulator, that is, one which can only transmit a current by violence and disruption.

The migratory and ionic theory of *liquid* conduction, and of the constitution of electrolytes generally, entered the field first, and,

although stoutly resisted by some chemists, appears to be holding its own, and to be invading one province of physical chemistry after another with marked success.

Materialising Tendency in Physics.

The ionisation doctrine and its many developments may be regarded as an encroachment of physics on the preserves of chemistry, since it has certainly modified ideas about the nature of solution; but there is a converse process now going on, and in the course of a sort of triumphant materialisation of obscure entities, achieved at any rate hypothetically and speculatively if not yet in any substantial manner, Chemistry seems to be dominating emancipated parts of Physics.

The latest and most astonishing attempt towards the reconversion of Physics into Chemistry appears in a brilliantly clever and apparently serious Address to Section A by Professor Callendar, this year, on the resuscitation of caloric or the material theory of heat—a theory which carries with it the ancient view that physical changes of state, such as vaporisation and liquefaction, are really the solution of matter in the substance of that apparently imponderable material caloric, and vice versa.

After this it is barely surprising to hear the biologists call upon the chemist to explain the phenomenon of life, and to produce in their glass vessels—if only they can stumble on the right environment, and on a judiciously combined assortment of material—some low form of living matter.

In view of the remarkable experiments recently made on the influence of various strengths of mere salt solutions in fertilisation and cross-breeding, it is not surprising that an anticipation of the kind should be promulgated. At present it is no more than a speculation, but if followed up, although it may not lead to the result anticipated, it may lead to others of perhaps equal interest.

The careful and accurate and painstaking and recording experimenter is always justified, and sometimes he is rewarded by results; but experiments of this kind, conducted in the dark as it were—that is, without a clue of theory—conspicuously need the utmost care; and concerning such experiments considerable scepticism is for a time legitimate and necessary. Of such kind, in that respect at least—I may incidentally mention—are some experiments and observations with which I have been more or less associated in connexion with what is known as psychical research. Positive results in this subject, when established, must be of extraordinary importance and novelty, but to establish them excessive care is

necessary, and until they are substantially verified respectful scepticism is entirely legitimate.*

Tendency to Return to Ancient Views.

All this tendency to return to discarded hypotheses and revivify old beliefs—for spontaneous generation is, I suppose, a very old belief or superstition—is a matter of great interest; and it is astonishing to find how much can still be said for ancient views. Forty years ago the Caloric theory of heat seemed dead beyond redemption, and I do not say that it yet lives, but the ingenuity of Professor Callendar finds a great deal to say for it, some of it of a cogent kind; it appears to be quite a possible mode of expressing facts, and one that is perhaps convenient for several non-elementary purposes.

At any rate, Professor Callendar's Address to Section A at Dundee confers on the abstract mathematical idea of *entropy* a local habitation and a name which I for one had never previously recognised, and which I fancy neither Rankine nor Clausius recognised either; whilst it emphasises, what was really never doubtful, the extreme brilliancy of Carnot's treatise on the motive power of heat. Moreover, it unifies the treatment of heat engines and electric motors, so far as can reasonably be expected without the opposition of sign familiar in electricity but presumably without meaning in heat. It is true that the production of fresh caloric during any irreversible process raises a difficulty about regarding heat as a substance; but, from Professor Callendar's point of view, the difficulty is by no means insuperable. The source of the substance can perhaps be traced as readily as we at present trace the source of *heat-energy* when that too is freshly generated by the like irreversible processes.

Then again in early days it was customary to jeer at the prevalent popular habit of speaking of electricity as a fluid, and until we knew more about it the practice was certainly to be deprecated; but now, in the light of further knowledge, something very like an improved and more definite fluid theory seems likely to hold the field.

Hitherto, Röntgen radiation has seemed to belong almost wholly

* When I speak of psychical phenomena as novel, I do not mean that testimony for their reality is limited to recent times—folk-lore legends about them are as old as humanity; the novelty consists in their now trying to make good their position in a scientific age, and in their appearing in a scientific dress. If we succeed in exposing them to rigid scrutiny, it will be another case of materialising the vague, the discredited, and the unseen. But that seems rather the tendency of science at the present day, and is noticeable in many branches, as I will emphasise later.

to Physics, whilst Becquerel radiation belonged largely also to Chemistry, to which science our friend the late Dr. Russell's radiation or emanation has always belonged wholly; but now judgment as to the nature of Röntgen rays may have to be regarded as open to revision.

We have already called attention to the fact that the undoubtedly corpuscular nature of some kinds of radiation, such as cathode rays, α-rays, and β-rays, has inevitably led to an attempt to resuscitate a corpuscular theory of light; and, if the anti-ether speculators who support the Principle of Relativity are to pave their way into anything approaching smoothness, some form of corpuscular light would clearly be necessary.

The Attitude to Established Laws.

General Physical Laws.

Amid this sea of conflicting hypotheses and guesses what should be our attitude? and how far should we condemn those philosophers who in their anxiety to stem the tide of materialistic philosophy (in which enterprise I for one am a sympathiser) have tried to throw doubt upon certain well-established and fundamental laws of physics—an enterprise wherein, as in duty bound, I part company with them.

I urge that our attitude should be this:

Let us admit that any law applicable to concrete objects (not merely to abstractions), and established by induction on a basis of experience, must necessarily be of the nature of a postulate; but let us hold some of the postulates as so well established and secure that any argument that would necessitate their overhauling is *ipso facto* to that extent discredited, and not to be countenanced unless supported by new and revolutionary facts; and even these new facts we must try to explain in harmony with all well-established laws, rather than as disturbing or negativing them.

In other words, let us seek to reconcile all new facts with the fundamental laws of physics, applied in a proper manner, until compelled to cast about for some higher generalisation. For in all probability that higher generalisation, when it comes, will be supplementary rather than superseding; and the conditions which necessitate its admission will be specifiable and definite when the subject is properly understood.

Among such well-established laws I should place first Newton's laws of motion; remarking that they apply to matter only, not necessarily to ether; and remarking also that effective *mass* may be variable under certain conditions,—as it often is, for instance,

simply enough, in the case of a falling raindrop, or of a sphere entering a perfect fluid.

Measurements of e/m, made on particles flying at two-thirds of the velocity of light, are by some said to invalidate Newton's second law. It is to my mind unquestionably preferable to express the fact in terms of variable inertia—the value of the inertia becoming in that case a known function of speed through ether.

Those who disbelieve in ether cannot, of course, agree with this dictum.

Again, the recently discovered *pressure of light* is sometimes said to invalidate Newton's third law. I should prefer to express the fact by saying that, when applying the law quite generally, an ethereal wave-front must be taken into account, as well as matter; and that we thereby get our first mechanical touch with the ether of space.

Supporters of the Principle of Relativity will consider this nonsense.

Another law I should place high and dry out of the reach of immediate controversy, is the Conservation of Energy.

In so far as the actions of living beings seem to conflict with this law, in so far as the facts of guidance and control appear to militate against it (as I for one hold that they do not), I would rather look for some new form of energy, or some ethereal seat of force or reaction, rather than doubt the generality of a comprehensive law of that kind. That law I should assume true; provided always that every form of energy, known and unknown, is taken into account.

Again, the conservation of matter, although it is a law that requires caution in its statement, and although the disintegration of material atoms is sometimes said to upset it, is probably true in essence. We must admit that our category of the thing conserved may have to be enlarged, so as to include electrons and other ethereal groupings or peculiarities, but it seems to me distinctly best to adhere to the idea of the conservation of fundamental substance until irrefragable evidence to the contrary is adduced.

All these laws may some day have to be revised, and at any time they may have to be more carefully formulated; but it is a mistake to be willing too easily to pluck them up and discard them. So it was once with the law of gravitation. Every new perturbation detected in astronomy was liable to raise doubts about the exactness of the index 2 in the statement of the law of inverse square. I do not say that such doubts were illegitimate, although they have proved unnecessary, but I do say that this mode of explanation should be only seriously contemplated when other

resources had failed; and as far as I know, other resources have not yet finally failed in any single case.

Among other postulates of high authority I should be inclined to place a wave theory of light—interpreted, of course, in terms of electricity and magnetism, not an elastic solid theory but definitely in terms of ether. For it seems to me that to try to discard the ether on the basis of a Michelson-Morley experiment, which after all is thoroughly and well explained by the FitzGerald-Lorentz hypothesis, is both retrograde and injudicious.

Relativity.

Some mathematicians, among them the late Professor Poincaré, are willing to give away their kindred subject of physics by admitting or maintaining that our laws are not important statements of fact, but are only conveniences of expression. And many philosophers seem eager to accept this vicarious generosity at their hands.

But such repudiation of our claims, and reduction of our life work to insignificance, I altogether deprecate. If we are not seeking real truth, if we are only seeking convenience of expression, the science of physics is not the noble structure which I for one think it.

To take the simplest and most rudimentary example:

Are we to suppose that it is only a matter of convenience whether we say that the earth turns on its axis, or that the host of heaven revolves round it once a day? I hold that the one is a genuine and absolute truth, whilst the other is a genuine and absolute falsehood; and that convenience of expression has nothing whatever to do with the matter, except that the truth must always be ultimately more convenient than error; just as I say that it is true that a train is travelling over the surface of the country, and not true that the ploughed fields and hedgerows are contorting themselves in the eyes of stationary travellers. The relativity of motion, thus pressed, and taking matter alone into account, is really absurd. Yet those who discard the ether are constrained to assert that there is no pragmatic difference between the two forms of statement, and no mode of ascertaining which is true: no meaning, in fact, in absolute motion at all.

On the other hand, those who accept the ether attach a definite meaning to motion through it, and are ready to admit as probable that in ordinary circumstances motion as great as the velocity of light can only be asymptotically reached; or at least that if it is reached or exceeded the first law of motion will, so to speak, break down, that is, become inapplicable, because to maintain the motion a propelling force will be required. Indeed, some day these

physicists with whom I agree expect to be able to measure the actual velocity of masses of matter through the ether of space by some definite phenomenon due to *this* kind of relative motion—which is not the kind contemplated by the Principle of Relativity. That principle would lead us to maintain that inasmuch as this kind of motion is meaningless it certainly can never be experimentally proved.

The great thing to avoid in science is negations. Let us make and substantiate positive assertions. But negative assertions—statements as to what does not happen, or what is not possible—although occasionally necessary, are always dangerous, and should be kept in rigorous check.

Life and Radioactivity.

Take, for instance, the attempts to construct living matter out of artificially combined materials. It may be impossible, but the attempt is quite legitimate, and no one can positively say that it will never be successful.

In so far as life demands energy for its peculiar manifestations and trigger-pullings, an available source of such energy can easily be suggested. It may or may not be a useful, that is, a true, suggestion, but the phenomenon of *radioactivity* indicates a possibility. We know now that atoms possess a store of energy which they give off in random directions as they periodically and spontaneously disintegrate. We have also long known, or supposed, that organic compounds left to themselves, apart from the cohering or integrating influences of life, likewise disintegrate and evolve energy —gradually passing down a series of stages, giving off emanations and heat, and ultimately becoming inorganic. A decaying heap of refuse, a pile of manure, represents to me a sort of chemical analogy to the physical activity of uranium.

The one is an affair of atoms, the other of molecules; but in order to be conspicuously radioactive the atom must be large and massive, whilst in order to exhibit organic instability to a high degree, the molecule must be large and complex.

In both cases there appears to be a complex grouping which, either with or without stimulus, disintegrates into something simpler, and generates heat or evolves energy in the process.

Here, then, is a stock of energy running to waste: it would seem eligible for guidance. What life has to do is to control this spontaneous disintegration of protoplasmic cells, to regulate the activity of the ganglia in the brain, for instance, or to suspend the disintegration of organic material until some appointed time, and then to direct it along a determined channel. That is all that a sports-

man or artilleryman does with the energy of gunpowder. He withholds its explosion until an appointed time, and then he liberates it in a definite direction. To say that he propels the projectile, and thereby conflicts with the conservation of energy, is absurd. This process of timing and aiming is typical of the control of life throughout. The manner and method by which life achieves this control, it is true, we do not yet know. It is one of the many things which we have to find out. But those who say that life cannot guide material processes unless it is itself a form of energy (which is false, a man is not a form of energy)—those who hold that life cannot, in fact, act at all unless energy is at its disposal (which is certainly true)—forget the apparently spontaneous activity of complex organised molecules, forget the atomic disintegration manifested by radioactivity. Energy is not a guiding or controlling entity at all. It is a thing to be guided. Energy by itself is as blind and blundering as a house on fire or a motor-car without a driver.

There is a great difference, moreover, between matter potentially living and actually alive. It must never be forgotten that in the physical universe our power is limited to the movement of matter: all that happens, after that, is due to the properties of matter and of its ethereal environment. If potentially living matter is ever artificially produced, by placing things in juxtaposition and bringing natural physical resources to bear upon the assemblage—which is all that we can do—then it may become alive. But if this last step is taken, it will be because something beyond matter, and outside the region of physics and chemistry, has stepped in and utilised the material aggregate provided—in the same way, presumably, as that in which it now steps in and utilises the material provided, say, in an egg or a seed. That is my belief, and only in that sense do I anticipate that the artificial incarnation of life will ever be possible. Certainly life has appeared on the earth somehow, and some day it may perhaps appear under observation. In that case it will be said to have been manufactured. It will be manufactured just as much as radium or radioactivity has been manufactured, and no more.

The spontaneous properties of matter, however, are far from exhausted: there may be many yet to be discovered. Twenty years ago no one knew or suspected the property of spontaneous radioactivity accompanied by atomic disintegration. Now it is a recognised commonplace of science.

Tendency to Discard Established Laws.

When radium was discovered many people jumped to the conclusion that the law of conservation of energy had "gone by the

board," and that there was not only mystery but "miracle" about the constant evolution of heat by a speck of radium salt. Miracle about it there is none, in any ordinary sense; and the mystery has reduced itself into a consideration of what is the best theory of the way in which electrons and the other atomic ingredients are grouped together, and as to whether their internal energy is due to their static configuration (as Lord Kelvin argued) or to their kinetic orbital movements, as others of us have urged as more explanatory and far more probable.

To suppose the law of conservation upset because a new source of heat is discovered—an unexpected intra-atomic store of energy opened up—is just one of those mistaken attitudes which I deprecate.

In the ether, so I believe, the amount of energy stored is immensely greater than anything which can be housed in a corresponding bulk of matter; and whenever humanity becomes able to tap this ethereal store, our descendants will be liable to go through the same revolutionary perturbation as some of us have gone through; unless they are wise enough to take warning by the past. Whether the ethereal source is being, by any means whatever, unconsciously tapped already, I do not know. There are a few observed facts which to me seem to hint at the possibility of such utilisation: but possibly the store of energy now known to exist inside atoms of matter is more than ample to account for anything of the kind.

Unification v. *Multiplicity of Causes.*

It is reasonable to enter a protest against entertaining the hypothesis of a multiplicity of causes for the same thing, without strong evidence that such multiplicity is necessitated by the facts. In some of the more complex, though it may be ordinary and familiar phenomena, a multiplicity of causes is obvious; for instance, to explain the death of an animal, or the fall of a house, or, again, such things as the settling of dust or of dew, the occurrence of wind, or the variation of terrestrial magnetism, several reasons can be given. But for fundamental things, one cause or one explanation must be expected to overpower and replace all the others, as soon as it is known; for instance, to explain magnetism, or light, or gravitation, or inertia, one explanation of each must surely be fundamental.

To illustrate the matter further: to explain the occurrence of a sound, hundreds of possible causes may be suggested; but to explain sound itself, a definite type of motion of the molecules is all that need be appealed to; and, whatever the kind or the origin of the

sound, the same kind of motion, in essentials, is all that we demand. Plenty of variety exists under the main head.

And this commonsense attitude I would adopt in cases where the explanation is not known. Thus, for instance, Larmor has shown that ethereal radiation must be generated by the acceleration of electric charges. If this be granted, as I think it must, the straightforward attitude is to seek to explain *all* radiation of an ethereal kind in that way, and to deny, except on definite evidence, that there is any kind of ethereal wave motion that cannot be traced to electronic acceleration.

Corpuscular radiation, however, undoubtedly exists likewise; and the question of to which category a given radiation belongs is perfectly open.

So also the more general and far more important and difficult question remains an open one whether in some not yet worked-out way a corpuscular radiation can be imagined which has all the essential properties of an ethereal wave or pulse; for in that case we may be able to recognise essential rightness in both points of view, and so be able to unify them—as has so often happened before in the history of science.

Alternative views are not always hostile and mutually destructive, although it sometimes conduces to the progress of science if their supporters think they are; but ultimately it may be found that they represent opposite aspects of a truth as yet imperfectly perceived. Certainly the fact that an advancing wave-front has momentum, exerts pressure, and sustains reaction—has, in fact, many of the properties of matter, except that it cannot rest—is calculated to attract attention and to give pause to anyone inclined to be dogmatic and dictatorial.

Again, J. J. Thomson showed in 1881 that an electric charge possessed the property of inertia, so that when moving it possessed momentum and kinetic energy. It was premature then to pay great attention to this curious and interesting result, which seemed to indicate that *mass* could be reduced to an electromagnetic or ethereal phenomenon; but now that electrons have been discovered, that is, electric charges so concentrated as to exhibit the properties of momentum and kinetic energy to a marked degree—and now that metrical experiments have shown that the electromagnetic part of their inertia is the whole of it, it becomes natural and proper to assume, in default of definite evidence to the contrary, that electromagnetic inertia is the only inertia that exists. That is very far from saying that electromagnetic inertia is thoroughly understood; all that the hypothesis or postulate does is to cause us to look for an underlying meaning for *mass* in ethereal proper-

ties, to regard the explanation of inertia as a possible quest for science, and not merely to sit down with folded hands and regard it as one of the fundamental and inexplicable properties of Newtonian matter.

If all mass is reducible to electric charge; if all radiation not of a projectile character is to be attributed to electric acceleration —of which ionic collision or chemical clash is one variety; if all electric currents are electrons or electric charges in motion; if all magnetism is due to the spinning of electrons; if all chemical affinity is really electric attraction over molecular distances—or, what is the same thing, if electrostatic attraction is chemical affinity a long way off—then clear statements of these various facts, when established, would be great generalisations and unifications, such as physicists used to strive for in old days and strenuously look forward to; although in these degenerate days mere convenience of expression is all that appears to be hoped for, and multiplicity of causes, like unexplained action at a distance, seems to be regarded with equanimity.

Meanwhile, I recommend these unified generalisations as postulates, as guides to inquiry, to be held, not dogmatically, but as working hypotheses; the burden of proof being thrown, not so much upon facts which support them—for those are manifestly numerous—as upon facts which render any of them uncertain. Such facts when adduced must be rigorously scrutinised, and not lightly accepted at their face value; still less, of course, must they be rejected as contrary to the laws of nature.

It may seem absurd that any facts could ever be rejected or excluded from contemplation on this latter ground, at this stage of the world's history, and with all the dogmatic errors of the past to guide us; but, nevertheless, I have reason for asserting that it is not so impossible as it ought to be.

Materialising Tendency throughout Science.

Discoveries in Biology.

The tendency of present-day science to materialise the invisible or to make concrete and tangible the vague influences previously thought of, has been well emphasised in a paper by Dr. Fraser Harris, of Halifax, Nova Scotia (see a paper called "The Metaphor in Science" in the American magazine called *Science* for August 30th, 1912).

The instances which he adduces are such as the following:

The "acidifying principle," or dephlogisticated air, called by Lavoisier "*the oxygine principle* for those who prefer the same

meaning in a Greek dress," is now the familiar oxygen, purchasable at so much per cubic foot, like timber.

So likewise Harvey in 1628 emphasised the probability of some movement in the blood—"movement as it were in a circuit"—*an motionem quandam quasi in circulo haberet.* He had begun to think whether there might not be such a movement, and later on had said "this motion we may be allowed to call circular"; thus the phrase "circulation of the blood" entered into physiology, although the actual fact was not visibly demonstrated until 1660—three years after Harvey's death. Then it became a concrete reality, and is now a common microscopic demonstration in the tissues of a frog's foot.

Again, the "animal spirits," supposed by Willis in 1650 to be driven inwards by the impression of an outside object, so as to give rise to sensation, and then to rebound from within outwards so as to excite movement, are now the constantly experimented-on nerve-impulses, the physical speed of which was measured by Helmholtz in 1850. Furthermore, the energy of even this nerve-impulse is being traced to minute granules or prisms alternately accumulated and consumed in the nerves, called after their German discoverer, *the granules of Nissl.* These appear to be the dynamogenic material widely distributed throughout the nervous system; and "nervous exhaustion," so far from being fanciful, is becoming associated with visible depletion of these microscopic granules.

Then, again, muscular fatigue, understood by most people as merely a particular kind of feeling or sensation, is now made concrete and shown to be the result of mild muscular poisoning, or the deposit of fatigue-toxins in the system.

As for malaria, a term which merely means "bad air," and ague, also vaguely called paludism or the influence of marshes, they are now traced, as everyone knows, to a parasite of the mosquito—traced, that is, to the bite of a thing which can be crushed with the fingers.

Plague or pestilence, also, was in ancient times attributed to various mysterious causes—such as a conjunction of the planets, the taking of a census, or the iniquities of the Jews—but it has now been proved due to a minute vegetable parasite inhabiting the fleas of rats.

The microbe of "influenza," even,—the very name for "influence"—has now been seen by the trained eye of the microscopist; and it is not to be doubted but that further progress in the same direction will be made.

Everywhere, as Fraser Harris well says, indefinite and elusive things have been identified and shown to have a local habitation

or a distribution in the recesses of the living body. *The whole tendency has been towards the objectifying of the subjective and the visibility of the unseen.*

It would lead too far away from the subject to speak of the way in which other vague and unseen entities or imaginaries, such as spiritual existences and phantasms, are being brought to book and materialised; nor are the facts yet ripe for public discussion; but in passing I may express my opinion that a materialising tendency is becoming conspicuous here also, and that ordinary mechanical acts and appearances will have to be directly attributed to ordinary or perhaps rather extraordinary mechanical and material causes, whatever their ultimate or indirect meaning may be. In even higher matters, I am convinced that progress lies in the direction of postulating definiteness and of thrusting vagueness out of the field. Skill and instinct are needed, however, to determine when it is time to move, and to discriminate genuine advance towards daylight from benighted blundering into a bog.

Demonstrations in Molecular Theory.

Another thing that has often been considered rather a vague matter of inference, and one on which a good deal of scepticism has persisted for a century, that is, since the time of Dalton—although the hypothesis in one form or another is as old as the Greeks—is the existence of those material discontinuities which are styled atoms. Although the atomic theory of chemistry has held its own, and although chemists have tried to picture to themselves the kind of atomic arrangement or grouping which would account for the observed properties of molecules—among other things for their crystalline interlockings and angular facets—yet chemists have always been careful to say that these pictorial representations were not to be taken literally or supposed to correspond with actual fact, but that they were to be treated in a more or less metaphorical or allegorical manner rather than as statements of reality. Indeed, the tendency was to doubt whether the actual *fact* of such arrangements could ever be perceived; and a good deal of scepticism persisted in the minds of at least a few chemists as to whether "atoms of matter" were more than a convenient verbal expression. It was clearly realised by physicists that atoms and molecules were of so minute a size as to be always beyond direct microscopic vision, since the waves of light, although exceedingly small, are much larger than molecules; and accordingly the eye, however much assisted, could never hope to see such things by aid of the comparatively coarse vibrations of visible light.

But that has not prevented the invention of the ultra-microscope,

whereby diffraction phenomena can be ingeniously arranged so as to show, in a sense, the appearance of things far below ordinary possibilities of vision.

Crystal Structure.

And now, quite recently, the announcement is made from Russia that by the use, not of visible or even ultra-violet light, but of ethereal pulses of immensely shorter wave-length—of pulses excited by the sudden stoppage of electrons, and therefore comparable in size rather to electrons than to atoms of matter—by the use, that is to say, of *X*-rays and a photographic plate—it has been possible to examine into and depict the actual molecular arrangement and interior architecture of crystals, whereby the anticipations and geometrical arrangements laboriously arrived at as probable, by the life-work of Mr. William Barlow, F.R.S., and by him in association with Professor Pope, appears likely to be verified, improved, and made definite.

Whatever may be the results achieved so far (and at present detailed information is lacking), the report is too probable to be disbelieved; and however incipient may be the method as at present realised, it can hardly be doubted that on some such lines definite progress will eventually be secured, and the invisible and hypothetical and mysterious once more be brought under actual and definite observation.

I base these anticipations on the diffraction photographs obtained recently by Drs. Knipping and Friedrich, and treated theoretically by Professor Laue; and also upon the testimony of Dr. A. E. H. Tutton, F.R.S., himself an eminent and experienced worker in crystallography. For he has described in a preliminary way discoveries made by Professor von Fedoroff, of St. Petersburg, confirmed apparently in the laboratories of Professors Röntgen and von Groth in Munich, whereby diffraction photographs of what he calls the space-lattice or molecular arrangement in the crystals of zinc blende can be obtained by the use of *X*-rays; the molecules and their actual arrangement in the crystal becoming visible, or inferable, and being such as apparently to confirm the independently discovered and identified types of homogeneous and symmetrical arrangements of the many classes of crystals studied with so much skill and pertinacity by our countrymen above mentioned. This, if it be a fact, will have to be recognised as a striking and admirable case of scientific prediction, the various crystalline structures and accuracy of characteristic facets having been indicated by theory long before there was any hope of actually seeing them; so that once more—always assuming that the heralded

discovery is substantiated—the theoretical abstraction will have become concrete and visible.

Brownian Movement.

But, after all, these are static things in comparison with certain discoveries of extraordinary interest developed during very recent years in connexion with the Brownian movement; whereby the kinetic theory of gases has been extended both theoretically and experimentally, and shown to apply, not to molecules only, but also to the spherical particles of a precipitate or liquid emulsion—particles which are perfectly visible in the microscope, and the movements of which can with care be projected on a screen for popular observation. I understand that, quite lately, they have been even kinematographed, by instantaneous photography, at intervals of 1/20th of a second.

These particles have been skilfully shown, by M. Jean Perrin, Professor of Chemical Physics in the University of Paris, to obey gaseous laws in complete detail; and, by measurements made on them, he has not only obtained determinations of the various gaseous constants and atomic magnitudes, but, in the light of the beautiful theory of Einstein, he has furthermore gained ocular evidence of the truth of a great many previously abstract and mathematically formulated laws.

For instance, Maxwell's law of the equipartition of energy—originally applicable to gaseous molecules considered as a system of elastic bodies colliding at perfect random—has been proved to hold in the case of these comparatively great masses, some of them as much as the hundredth of a millimetre in diameter, as well as to the atoms themselves; and certain molecular processes, such as coagulation or the formation of colloids, seem to be becoming visible by their means.

Some of these particles of which the Brownian movement has been observed are truly immense compared with atoms, since particles of ten microns (the hundredth of a millimetre) in diameter are as much bigger than atoms as atoms are bigger than electrons. Their osmotic pressure is less than the thousand-millionth of an atmosphere, but their atomic weight is such that if conceived of as a gas at normal pressure and temperature, and still subject to Avogadro's law, their so-called gram-molecule would amount to 200 thousand tons.

If M. Perrin's contentions are justified, it is, as he virtually says, rather singular to find the number of particles emitted by radium to be connected with Avogadro's constant; and this with the equilibrium distribution of particles in a liquid, and the distribution of

energy in the infra-red spectrum, as well as with many other things of extremely diverse character.

Furthermore, these particles can be shown to be disobeying the second law of thermodynamics, at least in a form in which it is often stated; since they rise sometimes in a lighter liquid, and thereby extract work from it, although the temperature is perfectly uniform and the liquid stagnant; thus showing—what indeed is well known—that the liquid is only statistically stagnant, whilst its individual molecules are in a state of strong agitation, and that the uniformity of pressure experienced by every side of a submerged body is only an average effect, true when the surface is sufficiently large for the law of averages to be valid. These particles are too small to satisfy this condition, and accordingly they are bombarded in an unbalanced manner, and move irregularly. But the behaviour of these particles also emphasises the fact, which appears to be less well known than it ought to be, that the second law of thermodynamics is essentially a statistical law, not a fundamental law of nature; it concerns practical methods of using the irregular and unorganised motion called heat. That is to say, the second law is only applicable when the terms *heat* and *temperature* are appropriate; and these terms are necessarily concerned with large groups of molecules, and have no ultimate meaning when individual particles are attended to, for then their heat energy may be conceived of as being as available as any other kind of motion energy, for instance. that of a piston rod or a flywheel.

Maxwell's Demons.

In the case of the Brownian movement the particles watched are small enough to demonstrate the bombarding influence of small groups of particles; and accordingly they behave somewhat as Maxwell's demons behave, except that they are purely inert and unintelligent—taking blows as they find them by chance, not looking for them—and therefore do not exert any demoniacal or discriminating influence the effects of which can be detected on a large scale; they require to be watched individually for any incipiently demoniacal occurrences to be observed.

And, further, it appears that the motion of these particles is so intricate and irregular, so polygonal and revolutionary and discontinuous, that no reasonable tangent can be drawn at any point of their path, so that they have suggested to M. Perrin—no doubt half-jocularly—the physical realisation of those curious curves, invented by mathematicians and hitherto supposed limited to abstract mathematics, which, although essentially continuous, have an infinitude of tangents at every point and no differential coefficient.

I doubt if physicists ever expected to be able to measure, still less actually to see, the effect of a single atom. But the extraordinary energy with which α-particles are ejected from a radioactive substance has now enabled this remarkable step to be taken. The ionising effect of a single particle, admitted through a minute orifice, is measurable by an electroscope; and the flash which it produces, when it strikes a target of sulphide of zinc, is popularly familiar in Crookes's spinthariscope.

The speed of these charged atomic projectiles, thus spontaneously ejected from radium by intra-atomic energy, is such that a milligram of matter travelling with the same speed could do as much damage as a one-and-a-half ton shot fired from a cannon.* So, knowing this, it is not surprising that, although only single atoms, they can make a crystal flash where they strike, or can ionise 86,000 molecules of air; but it remains still surprising to learn from Rutherford's measurements that a milligram of radium is continuously ejecting 34 million of such projectiles every second. Yet these are things about which scepticism is quite inappropriate.

Scientific Consequences of the Discovery of Radioactivity.

The discovery of radioactivity, developed as it has been by the labour of physicists still working in full blast, has resulted in such important consequences as the following:

1. Definite speculation as to structure of the atom.
2. Discovery of an immense quantity of intra-atomic energy.
3. A new kind of chemical change independent of any physical surroundings.
4. Transmutation of one element into others, and an estimate of the life-time of each.
5. A probable source for helium and the other inert gases.
6. The probable parentage of lead, and ultimately of other well-known substances.
7. Detection of the ionising power of rapidly-moving charged particles.
8. Calculation of the energy required to ionise an atom of a gas.
9. "The close connexion of the photographic and phosphorescent actions of the α-rays with their property of producing ions, raises the question whether photographic and phosphorescent actions in general may not, in the first place, be due to a production of ions in the substance."—(Rutherford.)
10. Data required for calculating the age of the earth supplemented so greatly that previous calculations are superseded.
11. Incipient computation of geological eras and dates.

* At a speed of 1700 feet a second.

12. A possible additional source of solar and stellar energy.

13. Ability to make observations on matter and electric charges moving with nearly the speed of light.

14. An experimental reduction of material inertia to electromagnetic and ethereal influence.

15. A method of gaseous analysis which exhibits not only the kind of substance, but its state of molecular aggregation, and likewise the electric charge which each molecule or group carries.

16. A method of determining atomic weights, even of very evanescent substances.

And the list can be extended.

Part II.—Historical.

Work of Henri Becquerel.

Henri Becquerel, born in 1852, lived from his infancy in the atmosphere of the laboratory of the National Museum of Natural History in Paris. At the age of nineteen he entered the École Polytechnique. From it he went into the Corps des Ponts et Chaussées, and studied as an engineer for three years. In 1875 he published a work which gained him a position as Demonstrator at the École Polytechnique, where he became Professor in 1895. In 1878, at the death of his grandfather, he became assistant in the Museum, under his father, then Professor; and him also he succeeded in 1892. He was admitted into the Academy of Sciences in 1889, at the age of thirty-six.

He was greatly attracted by Faraday's discovery of the action of magnetism on light, and considered that the department of magneto-optics was likely to be fruitful in discoveries. He seems to have detected a relation between the rotary magnetic power and the index of refraction of substances, the function being $\mu\sqrt{(\mu^2-1)}$, which he claims approximately for bodies belonging to the same chemical family. This was published in 1875. He found, however, afterwards that the law for magnetic substances is quite different from that for diamagnetic, the negative rotations varying approximately, not as the inverse square, but as the inverse fourth power of the wave-length, and, in the case of dissolved magnetic substances, as the square of the concentration.

Up to that time the Faraday effect had not been observed in gases, but with this law as a clue he was able to realise the magnitude of the effect to be expected in their case; and in 1878–1880 he demonstrated that gases enjoyed the same rotatory power as liquids and solids—oxygen, however, on account of its magnetic properties, being anomalous.

He was accordingly interested in the influence of terrestrial magnetism on the atmosphere, especially on the effect of a great thickness of magnetised oxygen on light; and as a preliminary he determined the intensity of the earth's magnetic field by its action on carbon disulphide. Moreover, at the International Congress on Electric Units he proposed this as an absolute standard of current strength.

He developed some theoretical views as to the cause of magneto-optic phenomena, and became specially interested in the discovery of Zeeman. The interest of this, indeed, deflected him for a time from his researches in radioactivity—which he had just himself discovered—since he thought that the Zeeman effect corresponded exactly with that magnetic molecular action which he had been looking out for; and he illustrated magnetic rotation, the Zeeman effect, and anomalous dispersion, by an ingenious experiment on sodium vapour. Electrons seemed to him just to fill the lacuna between ether and matter, and so to be of value in sustaining the vortex or spinning theory of magnetism which he favoured.

He seems to have told his son that he had looked for the Zeeman effect in 1888, as indeed Faraday had before him; but, in both cases, without theoretical guide, and without being aware of the kind of magnitude which they must be able to detect.

(Sir J. Larmor had anticipated the effect theoretically, but, supposing radiation at that time to be due to atoms rather than electrons, had found the calculated effect too small for observation. He had, in fact, corresponded with me on the subject, and, stimulated by him, I repeated Zeeman's experiment, and showed it at a *soirée* of the Royal Society immediately after the Amsterdam discovery.)

In 1879 H. Becquerel published a memoir on magnetic details in nickel and cobalt, and showed that ozone was more magnetic than oxygen; whilst nickel-plated iron became curiously magnetic after having been heated to redness.

With his father he made many experiments on the temperature of the underground soil, and verified Fourier's theory for the case of underground temperature.

He applied a discovery of his father in 1873—namely, that infra-red rays were able to extinguish certain kinds of phosphorescence—to a study of the bands of the infra-red solar spectrum, and likewise to the spectra of other substances, in particular of water, of the atmosphere, and of rare earths; likewise of numerous metallic vapours. The new field thus opened to spectrum analysis must have covered a range of wave-length more extensive than the whole of the luminous region and of the ultra-violet portion at that time known (1883–1884).

He specially examined the phosphorescence of uranium salts, and studied the spectrum of their phosphorescence which his father had discovered, attempting to give the law of distribution of these bands. The non-phosphorescent salts of uranium appear to have absorption bands governed by the same law, revealing an exceptional molecular constitution.

He studied the absorption bands of a great number of minerals, attending specially to the spectrum of didymium which Bunsen had observed in 1866, together with their variation with the plane of polarisation of the incident light.

From all this he argued that the absorption of a molecule is independent of the action of neighbouring molecules, and goes on as if the absorbing molecule were alone; so that if a crystal exhibits absorption bands corresponding with its various directions other than the axial directions, it must mean that other substances are present. The occurrence of neodymium and praseodymium verified these deductions.

Becquerel considered that this method of absorption spectra, applied to crystals, conferred upon the observer a power of mapping out their intimate constitution; and he likens it to observing the arrangements of furniture and movements of people who dwell in a glass house.

Some years later (1891) he described for the first time the spectra of the phosphorescence emitted by minerals when they are heated; and, by differences of duration and brightness, considered that he could detect different components; thus, in the natural course of things, he was led to his fundamental and most brilliant discovery, with which physicists have been concerned ever since.

Personal Account of his Chief Discovery.

The following is a paraphrase of Henri Becquerel's own account of the matter:

The idea of examining whether bodies could emit an invisible and penetrating radiation was suggested to me by the announcement of the first experiments of Röntgen. Poincaré showed the first radiographs of Röntgen at the Academy of Sciences in Paris on January 20th, 1896, and in answer to a question from me [Becquerel] stated that the source of the rays was the luminous spot on the wall of the glass tube which received the cathode stream. I immediately thought of examining whether this new emission was caused by the vibratory movement which gave rise to the phosphorescence, and whether all phosphorescent bodies could emit similar rays. At this epoch no one imagined it a spontaneous production of energy; it was natural to suppose that a transforma-

tion of energy must be going on. In other words, that energy must be supplied in order to get the radiation.

Becquerel seems to have mentioned his project to Poincaré, and to have begun a series of experiments the very next day. On January 30th Poincaré wrote in the *Revue Générale des Sciences* an article on Röntgen rays, in which he said:

"Thus it is the glass which emits the rays, and it emits them by becoming fluorescent. May we not ask, therefore, whether all bodies whose fluorescence is sufficiently intense may not emit beside luminous rays the *X*-rays of Röntgen, whatever may be the cause of their fluorescence? These phenomena would then be no more [necessarily] connected by [being the consequence of] an electric stimulus. It may not be very probable, but it is possible, and doubtless easy enough to verify."

This pronouncement seems to have started a considerable number of experiments.

Thus, for instance, M. Charles Henry placed on a photographic plate, enveloped in black paper, an iron wire with a few coins, and on one of the coins some phosphorescent zinc sulphide, and exposed the whole to Röntgen rays. On developing the radiograph he found that the shadow of the iron wire appeared lighter under the coin covered with zinc sulphide, and concluded that that substance had emitted rays through the metal on to the photographic plate. The experiment, however, was not convincing, and has not been confirmed. M. Henry made other experiments, such as one on the action of the rays emitted by hexagonal blende across leaves of aluminium and cardboard—an experiment subsequently developed by M. Troost.

Some experiments seem also to have been made by Monsieur Le Bon, which, however, M. Becquerel mentions only to discard, since he considers that they have been wrongly associated with his new phenomenon. They have to do with rays from luminous sources said to be capable of traversing metallic screens, but stopped by black paper. Henri Becquerel considered them all due to known causes, but to be arranged and described in so confused a manner as to mask the real reason of the observed facts; he says that it suffices to re-read, in the *Comptes rendus*, M. Le Bon's first publications to convince anyone that the author had no idea of the phenomenon of radioactivity. M. le Bon's experiments were also reviewed by MM. Niewenglowski, Lumière, and Perrigot, and were shown to have been due to infra-red rays—which are known to be able to traverse ebonite. Becquerel himself verified the completeness of these explanations, but says that one note of Monsieur Niewenglowski deserves attention, namely, this: A screen covered

with powdered calcium sulphide, after having been exposed to light, emits radiations which are able to impress a photographic plate through cardboard and black paper; and Becquerel goes on to say that he has repeated similar experiments, which are remarkable—possibly indicating the presence of either infra-red or ultra-violet rays of penetrating character—but that the phenomenon does not appear to be the same as that which constitutes radioactivity.

His own first observations on the radiating properties of the salts of uranium were published at the sitting of the Academy of Sciences on February 24th, 1896.

In the first series, photographic plates enveloped in black paper were exposed to the radiation of phosphorescent substances stimulated in vacuum tubes too slightly rarified to give *X*-rays; but the exposure given was insufficient to show any result.

In another series, bodies such as fluorspar, hexagonal blende, etc., excited in ordinary air by sparks, were applied to a covered photographic plate in the same way; but still they gave no result, either during or after excitation, although the exposure lasted several hours. He says he hesitated to try some beautiful preparations of phosphorescent sulphides or other salts which he possessed, in these circumstances, because of their deliquescence.

Nevertheless, in spite of the negative results obtained so far, he still built great hopes on experimentation with uranium salts, of which he says: I had formerly many opportunities of studying their phosphorescence as a sequel to the work of my father. These bodies, he goes on, appear to have a peculiarly remarkable molecular constitution, regarded from the point of view of phosphorescence and absorption.

Among the preparations of uranium salts in his possession there were some beautiful plates of the double sulphate of uranium and potassium, which he had prepared about fifteen years before. These crystals, unalterable in air, seemed entirely suitable for the projected experiment, but he happened to have lent them to his friend, Monsieur Lippmann, in connexion with his researches on interferential photography, of which the beautiful results are well known.

The same day, however, on which M. Lippmann returned those crystalline plates, Becquerel made the first successful observation; whence originated the whole series of his radiographic positive results.

He placed two crystals of the double sulphate on a photographic plate enveloped in a double sheet of thick black paper, putting under one of them a piece of silver; then he exposed the whole to the sun—a procedure which subsequent knowledge showed to be entirely useless—and after some hours developed the plate, and saw

a light impression corresponding with the silhouettes of the crystals, and a shadow of the piece of silver. The luminosity of uranium salts ceases in the one-hundredth of a second after exposure to light, so that it appeared quite necessary to maintain the luminous stimulus during the attempt.

He then repeated the experiment, interposing a thin sheet of glass or of mica in order to stop anything due to vapour or other chemical emanation. The same result was obtained, only feebler. These were the results communicated by him to the Academy of Sciences on February 24th, 1896.

On March 2nd, 1896, he described further experiments, where he showed that plates protected by aluminium 2 millimetres thick were not affected at all by a whole day's exposure to the sun unless a crystal of the uranium salt was added.

Other simple variations were described, and then came the opportunity for discovery. He usually affixed the uranium salt to the aluminium or other opaque coating by strips of gummed paper. He prepared some in this way on Wednesday the 26th and Thursday the 27th of February, and as on these days the sunlight was very intermittent, and the exposure quite unsatisfactory, he preserved the plates, fully prepared for subsequent treatment, in a dark cupboard, without developing them or removing from them the crystals of uranium. Fortunately, however, the sun did not shine on either of the two following days, and so he developed the plates on March 1st, expecting to find only very feeble impressions. On the contrary, they came out stronger than he had seen them before, and he perceived that the action had continued in the dark. He announced this fact to the Academy of Sciences at its sitting on March 2nd, and naturally proceeded to repeat the whole of the experiments without any exposure at all, subsequently concluding thus:

It thus appears that the phenomenon cannot be attributed to luminous radiations emitted by reason of phosphorescence, since, at the end of one-hundredth of a second, phosphorescence becomes so feeble as to become imperceptible.

So he announced the fundamental new fact of the emission of penetrating rays without apparent exciting cause. Either the diffuse light had long stored its energy in these substances, or else there was some phenomenon of a completely new order. In the first case the effect must gradually decay with time; and it was to the examination of that possibility that his next series of experiments were directed. He proceeded to keep crystals in complete darkness for years, and naturally the complete disproof of the alternative or slow decay hypothesis was a matter of time. Suffice

it to say that although the cause of the phenomenon was not then ascertained, the fact of apparently spontaneous radioactivity was definitely established.

It is doubtful whether with uranium salts alone anything more than a small fraction of our present knowledge of radioactivity could have been attained; but very soon after the first discovery, namely, on March 7th, 1896, Becquerel made the important and practically useful observation that the new radiation had the power of discharging electrified bodies, that is, of rendering the surrounding gas a conductor. He employed a gold-leaf electroscope, of which the leaves were examined by a microscope, and measured their rate of subsidence under the influence of various salts. The comparative ease and rapidity and metrical character of this method of examination induced Madame Curie to take as the subject of her Doctorial Thesis the measurement of the radioactive powers of an immense number of minerals, and so led her gradually to one of the most brilliant and striking discoveries of modern times, the whole representing a new epoch in our knowledge of atoms, and therefore in physico-chemical science.

Work of the Becquerel Family.

The name "Becquerel" is so familiar to students of physics, and it seems so natural that the name should occur in connexion with physical investigations throughout the past century, that we are rather apt to take the work for granted and neglect consideration of the personality behind the work. Moreover, when there are three or four workers of the same name, some care is needed to discriminate the individual.

As this is a Becquerel Lecture it may be convenient here, therefore, to make a kind of summary of the work of this eminent family, especially as they constitute a group notable from the point of view of Galtonian heredity.

The present Professor of Physics in the Natural History Museum in Paris, Monsieur Jean Becquerel, has made a convenient summary of the work of his ancestors, that is to say, of his father, grandfather, and great-grandfather, in an inaugural Address which he gave on the assumption of his inherited Chair; and this I shall make use of in the summary that follows.

The earliest and most prolific of the group of four was Antoine-César Becquerel, who, in the course of an exceptionally long life devoted wholly to Science, made a series of familiar discoveries, of which we are too apt to forget the origin. They lay chiefly in the direction of the voltaic pile, electrometallurgy, and the applications

of electrical knowledge to natural history, meteorology, and agriculture.

His son, Edmond Becquerel, succeeded him, and his researches are mainly connected with photography, spectroscopy, and phosphorescence.

Work of Antoine Becquerel.

The work of Antoine César Becquerel may be thus briefly summarised:

In 1819 Antoine Becquerel seems to have investigated piezo-electricity, or the electric manifestation displayed by minerals under pressure, generalising the observations of the Abbé Haüy very considerably; thus it was that he was led from the subject of mineralogy to that of electricity.

In 1823 he worked at thermo-electricity and the seat of the *E.M.F.* in a voltaic pile, being a strenuous supporter of what was called the chemical theory, and arguing against Volta and Davy.

In 1825 he was comparing the electric conductivity of different metals, and devised the first differential galvanometer for the purpose.

In 1829 (nine years apparently before Daniell) he invented a constant battery, explaining why the power of the ordinary voltaic cell fell off so rapidly, owing to deposits on the plate, and indicating the necessity of dissolving or avoiding such deposits. So he says the best results are obtained when the copper is plunged into a solution of copper nitrate, and the zinc into a solution of zinc sulphate; the two being separated by a membrane of gold-beaters' skin. A pile so constructed, he says, with each metal plunged into a separate vessel enclosing a suitable liquid, avoids the ordinary polarisation of the plates, whereby currents tend to be produced in the inverse sense to the main current. Professor Becquerel now says that sulphate of copper was as often used by his ancestor as the nitrate, and that this constant battery was then called a *pile cloisonnée*; although in an improved and more practical form it became universally known subsequently as the Daniell cell.

In 1846 he constructed the first silver chloride cell; and in the year following invented an electromagnetic balance for measuring electric currents—a glorified edition of which, designed by Viriamu Jones and W. E. Ayrton, is now set up at the National Physical Laboratory under Dr. Glazebrook at Bushey.

For forty years his work lay in the direction of applying his electrical knowledge to natural history, to agriculture, and to physiology. He also considered electrical effects in meteorology and other terrestrial manifestations; attending also to such subjects as the climatic effect of forestry on rainfall.

In 1850 he worked in electro-metallurgy, studying the deposits of many kinds of metals, and the conditions under which they could be obtained; among other things finding how to deposit nickel and cobalt.

In 1867 he discovered the phenomenon of electro-capillarity, and demonstrated its influence in connexion with endosmose and exosmose. He doubted the existence of the muscular currents discovered by Du Bois Reymond, and ultimately attributed them to capillary causes. He found an *E.M.F.* between different liquids separated by porous diaphragms; and at the age of eighty-seven he considered all this in relation to the phenomena of *life*.

He died in January, 1878, and only a few months earlier, at the age of ninety, published his last work, on the *E.M.F.* and the heat production of electro-capillary actions.

Work of Edmond Becquerel.

Some idea of the work of Edmond Becquerel can be thus given:

Edmond Becquerel, born 1820, became, at the age of eighteen, assistant to his father; and, stimulated by the discoveries of Daguerre, studied the production of electricity by light, and endeavoured to make an electro-chemical actinometer. Among other photographic discoveries he photographed the ultra-violet spectrum in 1842, and began the photography of colours. His coloured photographs had to be kept in the dark, where they have lasted seventy years, but they cannot be exposed to even diffuse daylight.

In 1843 he studied Joule's law of heat production by electric currents in liquids, and made a liquid rheostat for use with a differential galvanometer to measure liquid conductivities.

In 1846 he examined Faraday's magnetic rotation of light, showing that it varied inversely as the square of the wave-length, and he verified the magnetic properties of oxygen.

In 1853 he investigated the conductivity of hot gases, and measured furnace temperatures by photometric means, showing that they were not so high as had been supposed. (A development of this method has since been applied to the temperature of sun and stars.) He also constructed a thermo-electric pile with about one-third of a volt *E.M.F.*

But the work for which he is chiefly known is that on phosphorescence. This had been begun by his father in 1839; the phosphorescence having been excited by electric discharges.

In 1843, in his work on the ultra-violet spectrum, he examined its phosphorescent influence, and thus saw the dark lines in that

region of the spectrum which he had already discovered by photography.

In 1857 he described the preparation of many phosphorescent substances, with the region of the spectrum appropriate for exciting each. He also excited them by the induction coil, and in 1858 invented that beautiful instrument *the phosphoroscope*, with which naturally he made many observations.

In 1859 he showed that rarefied oxygen remained luminous some instants after the passage of a discharge—a phenomenon which, in the case of nitrogen, has been so admirably pursued recently by our Professor Strutt.

In 1869 he published a work on phosphorescence called "Light, its Causes and Effects," in two volumes; which book is said by Professor Becquerel to have been full of suggestions to young physicists on almost every page.

In 1872 he began to examine the phosphorescent properties of uranium, and in 1873 devised a method of studying the infra-red rays of the spectrum, by their power of extinguishing the phosphorescence of a screen coated with hexagonal blende on which they fell. This became the basis for his work in making isochromatic plates by the use of different absorbing substances and of chlorophyll; and, throughout, he applied his researches to meteorology and to the action of light on vegetation.

Conclusion.

The experimental labours of Henri Becquerel, based on the work of his predecessors, has been already dealt with. It lies chiefly in the domain of phosphorescence and spectroscopy, especially the absorption spectra of crystals. He concerned himself also with magneto-optics, and was the discoverer of the spontaneous radioactivity of matter.

Professor Jean Becquerel concludes his Address with some useful remarks on matters of general interest, especially concerning the association of a Chair of Physics with a Museum of Natural History. It appears that the creation of such a Chair was judged useful in 1838, after some of the work of his great-grandfather. A small and modest laboratory was then established, devoted to pure physics for the sake of its possible application to natural history of the most general kind. The discovery of radioactivity alone would have justified such a foundation, for the influence of that material property is now known in the ground, in mineral waters, in the atmosphere, and in geological formations; likewise in biology and medicine the rays have proved of high interest. But, as can be deduced from the preceding summary, a

great many other applications and practical consequences have followed from the researches conducted in that small laboratory.

Professor Becquerel claims that one of the causes conducive to the productiveness of this laboratory was the continuity of the work accomplished there. Antoine Becquerel began the study of phosphorescent substances under electric discharge. Edmond Becquerel continued the work, and recognised the exceptional properties of the salts of uranium. Henri Becquerel pursued the subject, and effected the climax. He himself definitely recognised the long tradition of pertinacious and successful inquiry on which he had built, and he spoke thus:

It was perfectly appropriate that the discovery of radioactivity should have been made in our laboratory, and if my father had lived in 1896 he it is who would have made it.

VAN'T HOFF MEMORIAL LECTURE.

Delivered on May 22nd, 1913,

By James Walker, D.Sc., Ph.D., LL.D., F.R.S.

The work of van't Hoff is indissolubly woven in the texture of the chemistry of to-day. Whether we are organic chemists, inorganic chemists, or physical chemists, we constantly utilise and apply his ideas, reap the benefit of the intense thought he devoted to the fundamental problems of our science. This is his splendid and enduring memorial. Nothing can add to it, nothing detract from it. Feeling this profoundly, I conceive that I may best discharge the honourable responsibility laid upon me by the Society if I give a sketch of his life, his main achievements, and his way of thinking with as little discussion and elaboration as possible, and as simply as I may.*

Jacobus Henricus van't Hoff was born in Rotterdam on the 30th of August, 1852. He came of pure Dutch stock, and his ancestry can be traced back to one Adriaen van't Hoff, who lived in the latter half of the seventeenth century at Groote Lind, near Rotterdam. His father was a practising physician in that city, his mother the daughter of a wine dealer of Middelharnis. The well-known landscape of Middelharnis, by Hobbema, in the National Gallery, shows the garden where van't Hoff often played in his boyhood.

Van't Hoff was sent to a private school, in which the education seems to have been of a liberal character, the usual scholastic subjects being relieved by sports, games, and physical exercises. Henry, as he was then called, to distinguish him from a brother likewise named Jacob, excelled in mathematics, and received commendation for his work in natural science. His mind, however, was not wholly occupied with his regular school studies, for at this time he was awarded prizes by a local musical society for singing and for pianoforte playing. Long country walks were a favourite recreation, and his letters show both his acute observation of nature and his keen appreciation of scenery. At the age of fifteen he entered the newly founded "Hoogere Burgerschool," a non-classical institution of the type of a German Real-schule.. Whilst constantly

* My information has been mostly derived from "J. H. van't Hoff's Amsterdamer Periode 1877—1895," by W. P. Jorissen and L. Th. Reicher (Helder, 1912), and in particular from the interesting biography by Professor Ernest Cohen, "Jacobus Henricus van't Hoff, sein Leben und Wirken" (Leipzig 1912). Both of these works contain full bibliographies.

near the head of his class, he never succeeded in reaching the first place, if, indeed, he ever tried.

Here he received his first instruction in chemistry. A school companion relates that they were taught according to the old system of formulæ, the formula of water, for example, being HO, although they were told in the highest class that a new formulation with H_2O was beginning to make headway. Practical instruction in chemistry was given in the school, and this evidently interested young van't Hoff, for he with some companions secretly repaired to the school on Sundays to finish their class exercises, and to perform additional unauthorised experiments. As they, boylike, enthusiastically chose to work with highly poisonous or explosive substances, their private investigations, when discovered, were brought to an abrupt end. Van't Hoff, however, continued his experiments at home, and conducted them on business-like lines, as he is reported to have charged spectators a small fee, which was expended in the purchase of fresh apparatus and material. A few months before van't Hoff completed his curriculum, the chemist Hoogewerff was appointed head of the school, and gave a sketch of the development of theories of organic chemistry, which, although too far advanced for the majority of the scholars, was welcomed and appreciated by van't Hoff. His leaving certificate reads as follows:

Mathematics and mechanics	Excellent
Physical science.....	Very good
History, etc.	Good
Languages and literature.....	Satisfactory
Drawing	Satisfactory.'

The following two years were spent by van't Hoff at the Polytechnic School of Delft. He had not yet decided what line of life he would take up, beyond that it should be practical. A holiday experience in a sugar factory, however, convinced him that technical chemistry was a somewhat monotonous occupation, and his inclination turned more and more towards pure science. He therefore on returning to the Polytechnic studied with increased zeal, and to such purpose that he received his diploma at the end of the second year, whereupon he left Delft for the University of Leiden.

What chiefly weighed with van't Hoff in moving to Leiden was the better opportunity afforded there for the study of the higher mathematics, the want of which he had greatly felt at Delft. At the University he frequented student society but little. On his rare appearances at the Debating Club, however, his comments on questions of the day and on topics of art or science provoked and enlivened discussion. Freedom and originality of thought were

even then characteristic of him. Indeed, he complained in later years of his University studies that they were too matter-of-fact, took too little account of his being a man and not a mere organ for the acquisition of knowledge; and declared that under their influence he would have become a dried and shrivelled scientific conglomerate had it not been for the counter influence of the intensely subjective and personal Byron. The writers who influenced him at this impressionable period of his life were, on the philosophic-scientific side, Comte and Whewell, on the literary side, Burns and Heine. But Byron was his favourite and hero. References to Byron, quotations from Byron, abound in his letters, and together with much verse in his native tongue van't Hoff wrote many Byronic stanzas in English.

Van't Hoff now definitely decided on the study and prosecution of chemistry as his work in life, and since Leiden offered no special facilities in the subject, he passed his candidate's examination, a necessary step towards the doctorate, and left the University at the end of a year.

Kekulé's fame attracted him to Bonn. The romantic surroundings of the Rhine University town made a strong appeal to him. He wrote later: "In Leiden all was prose—the town, the country, the people. In Bonn all is poetry."

Only a year was spent by van't Hoff in Bonn. That he became unsettled, melancholy, even bitter, is clearly shown by the tone of his letters. He found Kekulé unsympathetic, but made a lasting friend in Walthère Spring, of Liège.

There can be little doubt that Kekulé's teachings on the constitution of organic substances deeply interested van't Hoff, and it was on Kekulé's advice that he continued his scientific studies elsewhere instead of accepting a technological or teaching post. van't Hoff's choice fell on the "Ecole de médecine," in Paris, where the genial Adolphe Wurtz directed the studies of his enthusiastic pupils, but before proceeding to France he entered the University of Utrecht for three months in order to pass the doctoral examination preliminary to the doctorate. The most noteworthy circumstance of van't Hoff's sojourn in Paris is that there he made the acquaintance of the Alsatian, Joseph Achille Le Bel, who a year later was to share with him the credit of the invention of the asymmetric carbon atom. van't Hoff apparently did little in the way of practical research while in Paris, and it is recorded of him, "Il était si tranquille qu'on ne faisait pas grande attention à lui."

In order to obtain his doctor's degree, van't Hoff re-matriculated in the University of Utrecht in October, 1874, and was promoted to his doctorate in December of the same year. His dissertation

was entitled "A Contribution to our Knowledge of Cyanacetic Acid and Malonic Acid." It was of a routine character, and contained nothing beyond the powers of an ordinary advanced laboratory student. This is at first sight surprising, for van't Hoff had in the preceding September issued as a pamphlet his famous paper on space-formulæ. The original pamphlet was in Dutch, and bore the title, "An attempt to extend to space the present structural chemical formulæ, with an observation on the relation between optical activity and the chemical constitution of organic compounds." It argues well for the sound common sense of the young van't Hoff that he presented a humdrum piece of practical work for his dissertation rather than the startling innovation contained in his pamphlet, for the latter might have had an even worse fate than the equally famous thesis of Arrhenius, containing the first statement of the theory of electrolytic dissociation.

In giving this sketch of van't Hoff's educational career, I have made no attempt to treat it otherwise than in a superficial, mainly topographical, manner; and this because I fancy that the accidents of his education had little influence on his mental development. Now at the beginning of his productive career we find him a quiet, unassuming young man of twenty-two, with a physique by no means robust; reserved, but of agreeable manners; cultivated on many sides; with a taste for the writing of verse and for natural science, in particular entomology. He differed from the bulk of his academic contemporaries in being essentially a man of ideas, a thinker. He had pondered over the properties of the atoms, on their actions on one another at small distances, and over the problem of how the chemical and physical properties of compound molecules were to be conceived as a function of the nature of the constituent atoms and of their arrangement. The first tangible result of this cogitation was the laying of the foundation of stereochemistry.

It is a constant phenomenon, and always a fresh surprise in the history of science, to find a pioneer, capable, one might think, of any mental step, stopping short by a hand's breadth of some important discovery or generalisation. The driving force of the original idea exhausts itself, or the general state of knowledge fails in some particular, and years may have to elapse before a fresh mind with a new stimulus, and possibly a different goal, can take the required step. The early history of stereochemistry illustrates this peculiarity of scientific advance in striking fashion.

In a lecture published in 1860 Pasteur said: "We know, on the one hand, that the molecular structures of the two tartaric acids are asymmetric, and, on the other, that they are rigorously the

same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron? We cannot answer these questions." The ideas of the quadrivalent carbon atom and of molecular structure based upon it were still too novel and also too remote from Pasteur's practical line of thought, to enable him to take the short but, as it turned out, difficult step to the asymmetric carbon atom.

That the necessity for space-formulæ became increasingly felt is evident from the following quotations.

In 1867 Kekulé wrote: "The incompleteness of the old models may be avoided if, instead of arranging the four affinities of the carbon atom in a plane, we place them in the directions of hexagonal axes, so that they run out from the spherical atom and end in the planes of a tetrahedron."

A definite example of the use of space-formulæ is given by Paternò in 1869, who writes as follows:

"Three isomerides, $C_2H_4Br_2$, supposing that they really exist, can be easily explained, without the necessity of assuming with Butlerow a difference amongst the four affinities of the carbon atom, if we postulate that the four valencies of the atom of carbon are arranged in the sense of the four angles of a regular tetrahedron: then the first modification would have the two atoms of bromine (or any other univalent group) attached to the same atom of carbon; whilst in the other two modifications, the two atoms of bromine would be each attached to a different carbon atom, with the difference that in one case the two atoms of bromine would be symmetrically arranged, and in the other not."

Wislicenus in the same year clearly indicates the general nature and mode of solution of the problem in connexion with the lactic acids: "Facts like these will force us to explain the difference between isomeric molecules with the same structural formula by means of a different arrangement of their atoms in space, and to seek for definite ideas concerning this," a statement which he reiterates and emphasises in 1873.

These definite ideas were given practically at the same time by van't Hoff and by Le Bel, the former publishing his pamphlet in September, 1874, and the latter a paper in the *Bulletin de la Société Chimique* in November of the same year. One would naturally imagine that the idea which gave the key to the problem must have originated in one of the frequent discussions in Wurtz's laboratory, for here we have two young men parting at the end of June, and a few months later publishing separately a notion which was at the time generally regarded as something entirely novel and

revolutionary. Yet van't Hoff tells us that no communication on the subject had passed between them. He says: "That shortly before this we had been working together in Wurtz's laboratory was purely fortuitous; we never exchanged a word about the tetrahedron there, though perhaps both of us cherished the idea in secret. To me it had occurred the year before, in Utrecht, after reading Wislicenus's paper on lactic acid."

In view of the passages I have quoted above from earlier workers, it might almost be asked: What, then, did van't Hoff and Le Bel discover? Wherein lies the merit of their work that they should be acclaimed as the originators of stereochemistry when the problem and the fundamental ideas seem to have been so clearly enunciated before them? On the one hand, the idea of the asymmetric structure of optically active molecules was given by Pasteur; on the other, Paternò uses tetrahedral carbon atoms to explain a case of isomerism in much the same way as they would be used to-day, except that he regards the carbon tetrahedra as not being capable of rotation round the axis joining their centres. Separate, these ideas remained unproductive; correlated, they became endowed with marvellous fertility. Van't Hoff and Le Bel's great contribution to stereochemistry was to define the conditions under which the asymmetric structure appeared, namely, when the carbon atom was attached to four different groups. Van't Hoff, in addition, boldly adopted the tetrahedron as the formal representation of the carbon atom in this new aspect; Le Bel, whose considerations are more general, only mentions it once in his paper. Not only did they state the bare principle, however; they showed it was a living one, drew deductions from it, applied it on all sides, and delivered it, in short, as an effective instrument into the hands of their fellow-workers in chemistry. Otherwise, like Avogadro's principle, it might have been forgotten, and for years perhaps have awaited some Cannizzaro to rediscover or revivify it.

It is of interest to quote van't Hoff's own words as to the origins of his conception and that of Le Bel, and as to the points in which they differed:

"On the whole, Le Bel's paper and mine are in accord; still, the conceptions are not quite the same. Historically, the difference lies in this, that Le Bel's starting point was the researches of Pasteur, mine those of Kekulé.

"The researches of Pasteur had made plain the connexion between optical activity and crystal-form, and had led to the idea that the isomerides of opposite rotatory power correspond with an asymmetric grouping and to its mirrored image. Indeed, the possibility of a tetrahedral grouping was suggested. Le Bel closely follows Pasteur,

then, when he sees this grouping in the four atoms or radicles—inactive bodies all different—united to carbon.

"My conception is, as Baeyer pointed out at the Kekulé festival, a continuation of Kekulé's law of the quadrivalence of carbon, with the added hypothesis that the four valencies are directed towards the corners of a tetrahedron, at the centre of which is the carbon atom.

"Practically our ideas, so far as they concern the asymmetric carbon, amount to the same thing—explanation of the two isomerides by means of the tetrahedron and its image, disappearance of this isomerism when two groups become identical, through the resulting symmetry and identity of the two tetrahedra."

Le Bel's general treatment was more purely geometrical and in certain ways more thorough than that of van't Hoff, which was better calculated to appeal to chemists, and, indeed, gave the stamp to stereochemistry in its subsequent development. In detail the following points of difference between the authors may be noted. Le Bel accounts for the existence of internally compensated inactive forms, such as mesotartaric acid; van't Hoff, by means of the tetrahedra, clearly explains the nature of unsaturated inactive isomerides, such as maleic and fumaric acids.

The following lines contain a brief résumé of the original pamphlet of September, 1874. Van't Hoff shows that if we imagine the four affinities of the carbon atom to lie in a plane, the groups attached to them being fixed, and their positions not interchangeable, a great many more isomerides are predicted than actually exist. If, on the other hand, the affinities are not in a plane, but directed to the summits of a tetrahedron from its centre, the number of compounds predicted in general coincides with the number of compounds existing. His chief statements are given in the following terms:

(*a*) If the four affinities of a carbon atom are satisfied by four different univalent groups, two and not more than two tetrahedra are obtained, of which one is the mirror image of the other and cannot be superposed on it; that is, we encounter two isomeric structural formulæ in space.

(*b*) Each carbon compound which in the dissolved state effects a rotation of the plane of vibration of a polarised ray, contains an *asymmetric* carbon atom, that is, one whose affinities are satisfied by four different univalent groups. As examples, he gives lactic acid, aspartic acid, asparagine, and malic acid, with one asymmetric carbon atom; tartaric acid with two; the sugars, mannitol, etc., with at least one. Further, camphor and borneol, according to Kekulé's formulation, contain an symmetric carbon atom, and are correspondingly active.

The derivatives of optically active compounds lose their activity if the asymmetry of all the carbon atoms disappears; for example, inactive maleic acid from active malic acid, inactive succinic acid from active tartaric acid, inactive cymene from active camphor.

In a list of compounds the formulæ for which contain an asymmetric carbon atom, there are many cases in which the compound is not active. This may be accounted for in one of the following ways:

1. The compound may be an inactive mixture of two equally and oppositely active isomerides.

2. If the activity is small, it may be lost in the experimental error.

3. The condition "asymmetric carbon atom" may not in itself be sufficient, the nature of the different groups being of moment as well as their mere difference.

The principle that an optically active compound probably contains an asymmetric carbon atom gives the means of choosing between possible formulæ; for example, optically active primary amyl alcohol must have the formula $(CH_3)(C_2H_5)CH\cdot CH_2\cdot OH$. There is a certain degree of probability that an inactive compound contains no asymmetric carbon atom. Thus, the formula of citric acid is probably $CO_2H\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH_2\cdot CO_2H$, and not $CO_2H\cdot CH(OH)\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$.

Formulæ are given for the simplest optically active monohydric alcohol, monobasic acid, dihydric alcohol, saturated hydrocarbon, and aromatic hydrocarbon; and attention is drawn to the fact that there are no optically active normal hydrocarbons, alcohols, or acids.

(*c*) If two doubly bound carbon atoms are each united to two radicles which differ from each other, two isomerides, hitherto unforeseen, are predicted; for example, maleic and fumaric acids.

In van't Hoff's pamphlet the carbon tetrahedra are figured exactly as they are met with now in text-books of organic chemistry.

A French translation of the paper appeared soon afterwards in the *Archives Néerlandaises*, and a condensed French account in the *Bulletin de la Société chimique*. Finally, a much expanded French pamphlet, "*La chimie dans l'espace*," was published at Rotterdam in May, 1875.

Disappointment followed the publication. Instead of his hypothesis provoking discussion, as he had hoped, it was received by the majority of chemists with indifference, if not with coldness. Wurtz, Spring, and Louis Henry wrote warm acknowledgments of its receipt, but made no attempt to discuss or criticise. Berthelot, whilst admitting the general interest of van't Hoff's formulæ, took

up the ground that a complete representation of constitution involved a representation of the rotatory and vibratory movements of the atoms and groups, and was disposed to attribute optical activity to these movements. The physicist, Buys Ballot was the first to give serious attention to van't Hoff's theory, and in the *Maandblad voor Natuurwetenschappen* he published an open letter to van't Hoff, who replied in a paper (November, 1875), discussing many interesting points which had been raised in the letter. He gives, for example, the configurations of the ten isomeric saccharic acids. A cordial letter from Wislicenus then followed, suggesting that the pamphlet should be translated into German, which was done by Herrmann, and issued in 1877 under the title *Die Lagerung der Atome im Raume*, with a preface by Wislicenus. The German version, which differs in many ways from the original, was widely read, and van't Hoff's ideas now began to gain ground. Strenuous opposition by Kolbe, who at that time was tilting at graphic formulæ of every sort in a eries of lively articles in the *Journal für praktische Chemie*, perhaps, if anything, increased their vogue by drawing more attention to the subject.

Meanwhile van't Hoff had graduated, and was on the look-out for a situation. He failed to obtain any teaching post as science master in a school, but in March, 1876, he succeeded in becoming assistant in the Veterinary College of Utrecht, there to teach chemistry and physics. He had command of good apparatus, and during the two years of his tenure of the office he worked at a variety of subjects, the substances obtained from storax claiming much of his attention. He wrote several stereochemical papers, one on carbon rings, one on Ladenburg's benzene formula, one on the direction of the valencies of the nitrogen atom, and one on the connexion between optical activity and constitution.

To this period belongs his book, "*Ansichten über die organische Chemie*," the preface of which is dated Utrecht, October, 1877. In itself the book is almost unreadable, but it affords the clearest evidence of the author's independence of thought, his keen eye for essentials, and the painstaking way in which he sought to isolate materials and problems of pure chemistry from the traditional associations which obscured them. The first part is purely systematic, and treats of the physical and chemical properties of organic substances regarded and classified as derivatives of methane. In the introduction to the second part (published in 1881), he expresses himself as follows:

"The purpose of the second part is to obtain a knowledge of the chemical nature of carbon in itself and of the changes which it undergoes when the element combines with other atoms or

groups of atoms. To succeed in this purpose we must obtain a general view of the chemical reactions in which the carbon atom plays a part, and the changes in physical character which accompany them. If such a reaction is expressed by the general equation:

$$(\equiv C)X + Y{\cdot}Z = (\equiv C)Y + X{\cdot}Z,$$

the knowledge of the reaction must include a knowledge of the heat change which accompanies the reaction, and of the velocity with which it takes place under given conditions, whilst a knowledge of the changes of property is attained by comparison of the physical nature of $(\equiv C)X$ and $(\equiv C)Y$. The reaction expressed above in general form may be followed out for particular carbon compounds $\left(\begin{smallmatrix}\alpha\\ \beta\\ \gamma\end{smallmatrix}\!\!\equiv C\right)X$ in the same two directions. What ultimately appears as independent of α, β, γ is the expression of the chemical nature of carbon in itself; the difference due to the changes of α, β, γ are, on the other hand, regarded as the changes which carbon undergoes when it combines with other atoms or groups of atoms."

In the text of the second part we find the beginnings of those studies in chemical thermodynamics and affinity which were afterwards pursued to such good purpose.

In September, 1877, van't Hoff was appointed lecturer in chemistry in the Town College of Amsterdam, which a month later was raised to the dignity of a State University. In June, 1878, at the age of twenty-six, he became ordinary Professor of Chemistry, Mineralogy, and Geology; and six months later he married Johanna Francina Mees, the daughter of a Rotterdam merchant, whom he had known from early youth.

Van't Hoff spent eighteen years in the University of Amsterdam. Although the old laboratory in which he worked was small and inconvenient, he refused a call in 1887 to the newly created Chair of Physical Chemistry in Leipzig, eventually filled by Ostwald. His teaching duties were onerous. With two assistants he had to give instruction in organic and inorganic chemistry, crystallography (which he had studied with Groth), mineralogy, geology, and palæontology, and to conduct practical classes for 100 medical and 20 science students. Notwithstanding this, the amount of practical work he executed and supervised was very great. The atmosphere of his laboratory may be described in the words of his assistant, van Deventer. "Whoever knows the Amsterdam laboratory knows that things do not take place there in any ordinary way. There is something mystical, something uncanny in the air. And this demonic something is the belief—one might call it the superstition if success had not so often followed it—the belief of van't Hoff that his fundamental idea, the analogy between chemical

and physical phenomena, is profoundly true." Elsewhere van Deventer says: "It must be said that van't Hoff's work is in many ways more French than German. Soundness and solidity he certainly values, but he is in love with the idea in its general form, and his proofs are directed more towards establishing his idea in the world as a great rough block that cannot be overthrown, than to modelling and rounding it off—that he willingly leaves to others.

"This love of the idea is often found, too, in the experimental method which he adopted. Transition points were studied with an instrument which a well-trained physicist would only have used for preliminary experiments. Van't Hoff used it for the decisive investigation, and the proof is unimpeachable."

It is characteristic of van't Hoff's devotion to the idea that he chose as the subject of his inaugural address in Amsterdam, "The rôle of Imagination in Science," and strove to show how great a part imagination played in scientific investigation. He drew attention to the imposing number of scientific men with a leaning towards poetic and romantic invention, and closed his address with a quotation from Buckle: "There is a spiritual, a poetic, and, for aught we know, a spontaneous and uncaused element in the human mind, which ever and anon, suddenly and without warning, gives us a glimpse and a forecast of the future, and urges us to seize truth as it were by anticipation."

Following out the line of thought already indicated in his introduction to the "*Ansichten*," van't Hoff investigated various types of reaction velocity and chemical equilibrium, which he collected in his *Etudes de dynamique chimique*, published in 1884. It is true that much had been done by others in these fields of investigation; for example, in velocity by Harcourt and Esson and by Goldberg and Waage, and on the thermodynamical side by Horstmann and by Willard Gibbs, although the work of the latter was then unknown to van't Hoff, as indeed it was to chemists generally. Van't Hoff, however, systematised, exemplified, and applied the principles involved, and, in fact, left the subject of chemical dynamics much in the state in which we find it to-day. For example, he classified reactions into unimolecular, bimolecular, termolecular, according to the number of molecules taking part in the transformation. He showed how to determine the number of molecules taking part in a chemical action, and investigated secondary actions and disturbing influences. He discussed "temperature of inflammation." He introduced the symbol $\rightleftarrows$ for reversible actions. He introduced and illustrated the term "transition point," and showed the close analogy between the chemical "transition point" and the physical melting point, in

particular as regards the effect of pressure. He stated clearly the *principe de l'équilibre mobile* as follows: "Every equilibrium between two systems is displaced by fall of temperature in the direction of that system in the production of which heat is developed." He showed that Berthelot's *principe du travail maximum* is only strictly true at the absolute zero. Finally, he devoted the last section of the book to a study of chemical affinity. He shows how affinity may be measured by electromotive force, how at a point of transition the work of affinity is zero, and constantly uses the important equation:

$$\frac{d \log_e K}{dT} = \frac{q}{2T^2},$$

although he does not prove it, merely stating that it had been deduced in a rigorous manner from the principles of thermodynamics. I remember having read these *Études* in 1885 or 1886, and I can well recall the mingled feeling of revelation and bewilderment which the book produced on me. I had perused such books on theoretical and physical chemistry as were then available, but had derived comparatively little satisfaction from them. Here, I thought, was the real thing at last, hard to comprehend, certainly, but something definite. What I understood was excellent. What I did not quite succeed in understanding seemed, somehow, even better.

Arrhenius, at that time personally unknown to van't Hoff, in reviewing the *Études*, wrote as follows: "This work, which is of the greatest interest, consists of two essentially different parts: the first experimental, the second theoretical. The former is, however, of quite subordinate significance, notwithstanding the many peculiar and interesting phenomena discussed in it. In the latter portion the author displays an extraordinary talent for bringing a great series of different facts under one point of view, and he succeeds with relatively scanty experimental material in developing an imposing and harmonious scheme for the whole subject of chemical influence and action. Although the author has already gained a great name by his power of wresting secrets from Nature, his former efforts are placed entirely in the shade by this work. An enormous perspective has been opened up for future investigation. There are, however, but few workers in the promising field, though possibly this will shortly be remedied; for since Helmholtz, who sets the fashion in physical circles, has turned his attention of late years to such subjects, it will probably not be long before eager investigators are working at them."

A few years later this prediction was fulfilled, chiefly through the

instrumentality of Ostwald, the first occupant of the chair of physical chemistry in Leipzig.

In the *Études* we have the first appearance of osmotic pressure from the physico-chemical point of view. Through his distinguished countryman, the botanist, Hugo de Vries, van't Hoff had become acquainted with Pfeffer's osmotic measurements. He at once saw the thermodynamic importance of the conception, and used it in conjunction with the lowering of vapour pressure to calculate the affinity of certain salts for their water of crystallisation. In the following year (1885) he published in the *Archives néerlandaises* a paper bearing the title "*L'équilibre chimique dans les systèmes gazeux ou dissous à l'état dilué, gazeux ou dissous*"; and in 1886 he published in the Transactions of the Swedish Academy three memoirs, entitled "*Lois de l'équilibre chimique dans l'état dilué, gazeux ou dissous,*" "*Une propriété générale de l'équilibre chimique,*" and "*Conditions électriques de l'équilibre chimique.*"

In these papers van't Hoff had arrived at the complete analogy between gases and substances in dilute solution. He tells us that in giving the proof of his equation:

$$\frac{d \log_e K}{dT} = \frac{q}{2T^2},$$

by means of reversible cycles for dilute gaseous systems, it occurred to him that with the help of semi-permeable membranes all the reversible processes which make the application of thermodynamics to gases so simple might as readily be applied to substances in dilute solution. It at once followed that the osmotic pressure must vary with the temperature according to Gay-Lussac's law. Pfeffer's measurements for 1 per cent. sugar solutions seemed to confirm this conclusion, although they were scarcely sufficiently accurate to afford absolute proof of the relation. Then Pfeffer had shown that the osmotic pressure was proportional to the concentration, that is, Boyle's law was followed as well as Gay-Lussac's, and it was possible to write for dilute solutions an equation similar to that for gases, namely:

$$PV = RT.$$

The only thing left was to calculate R, the solution-constant, and compare it with the gas-constant. van't Hoff did this for sugar solutions from Pfeffer's measurements, and found to his surprise that the value was identical with that of the gas-constant. At first he looked upon this identity as a mere coincidence, but further consideration showed it to be fundamental, and that osmotic and gaseous pressure were always equal, when molecular concentration and temperature were equal, that, in short, Avogadro's law held without alteration for substances in dilute solution as well as for

gases, and that the molecular weights of dissolved substances could be determined on the same theoretical grounds as those of gases.

Raoult had in the meantime shown empirically how molecular weights might be determined from the lowering of the freezing point, and van't Hoff was now in a position to give the theoretical justification of this method, by deducing thermodynamically from Avogadro's law and the properties of the solvents, the quantitative rules for the lowering of vapour tension, the depression of the freezing point, and the elevation of the boiling point of solutions.

It should be noted that van't Hoff was from the first very careful to point out that all these relations were strictly applicable only to very dilute solutions, to "ideal solutions," as he calls them, and that he never claimed the theory of osmotic pressure as a complete theory of solutions. He definitely stated, indeed, in his address to the German Chemical Society (*Ber.*, 1894, **27**, 15): "It is not even necessary to choose osmotic pressure as the starting point [of these relations]; the whole might be deduced as readily from Henry's law or from Raoult's law. Only osmotic pressure is a very simple and handy expression for the whole behaviour, and its physical meaning is very readily stated and grasped, thus: If a substance in a state of dilution exists in surroundings into which it can expand by diffusion, then, at a given temperature, the pressure which will prevent this diffusion is dependent only on the number of dissolved molecules, and not on the nature of the medium." To van't Hoff's mind the real theory of the intimate nature of solutions begins where the simple laws *cease* to be obeyed. In a sense this is true, and a good example of what it means is afforded by the early history of the osmotic pressure theory. Van't Hoff had found that the value of the osmotic constant was not for all substances equal to the gas constant R. With his customary skill in handling such matters, he wrote the equation for these substances as follows:

$$PV = iRT,$$

using a factor i, which was thus the measure of the abnormality of the substance. The work of Arrhenius supplied two years later the explanation of the abnormality in the case of the great class of electrolytic solutions. The abnormally great value of i for such solutions was held by Arrhenius to be due to the molecular concentration in such solutions being greater than had theretofore been accepted. According to his theory of electrolytic dissociation, some of the original dissolved molecules had split up under the influence of the solvent into simpler positive and negative ions, so that the total number of molecules was increased, the excess of i over 1 being the measure of the increase. This, then, is a contribution

to the theory of solution for a certain class of solutions, and it appears to me that every future contribution will be of the same nature, dependent on the nature of the solvent and dissolved substance, and therefore of a different scope entirely from van't Hoff's generalisation.

Two distinct points may be noted in connexion with the papers just referred to. First, there is the introduction of the conception of osmotic pressure into thermodynamics generally, and the use of semipermeable membranes for reversibly changing the concentration of solutions. Second, there is the special application of the conception in deducing the simple general laws for ideal solutions. As van't Hoff himself has said, it would be possible to substitute for osmotic pressure in the purely thermodynamical treatment some other magnitude which is proportional to it, but it may be confidently predicted that the conception once introduced, and through which such advances have been made, will never be discarded.

One often encounters among chemists the impression that van't Hoff was essentially a mathematician, or at least a man of mathematical formulæ, who cared nothing for atoms or molecules. Nothing could be further from the truth. Van't Hoff's actual knowledge of mathematics is surpassed, I fancy, by the average honours B.Sc. student of to-day. His ability in this direction lay rather in the power of handling the mathematical tool for his own purposes. But, as is apparent from the passages I have already quoted, the essential thing for him is the reciprocal action and influence of atoms and molecules. The nature of osmotic pressure, as well as its law, was of profound interest to him. He first of all conceived it as having its origin in the mutual attractions of solvent and solute molecules, but soon discarded this view for one of molecular bombardment in analogy with the kinetic theory of gases. This kinetic theory of the origin of osmotic pressure, despite criticisms, still seems superior to any other that has been proposed, and awaits further development.

Although, as has been said, the papers comparing dilute substances with gases were published in 1885, it was only in 1887 that the ideas became generally known. Ostwald, the organiser of the campaign in favour of the new ideas of van't Hoff and Arrhenius, associated himself with the former in founding the *Zeitschrift für physikalische Chemie*, in the first volume of which the fundamental papers of the two pioneers of modern physical chemistry appear.

With the foundation of this journal van't Hoff's scientific life may be said to have reached its climax. His fame became world-wide, and many honours awaited him. A new chemical laboratory, built according to his designs, was opened in 1891, and many

foreign students visited him who could not have been accommodated in the old building. With the increase of his department, van't Hoff found that he had to devote more and more time to administrative duties, as is the universal experience of the heads of large laboratories. He naturally disliked to see his leisure for personal research slip away from him, and asks, "Besides men whose duty it is to teach, and who, if they have time and inclination for it, may prosecute research, is there not room for another class of men whose duty should be to investigate, and who, if they pleased, might also teach?" In the spring of 1895 a position of the latter kind was offered to him in Berlin. Great efforts were made by his colleagues in the University of Amsterdam to induce the Government of the Netherlands to retain him in Holland on similar terms, but these efforts were unsuccessful. Van't Hoff, in the spring of 1896, moved to Berlin, as a member of the Prussian Academy of Sciences and as a Professor in the University. His academic duties were of the lightest, one lecture a week being all that was required of him. His research work was carried out in a small laboratory situated in a pleasant suburb of Berlin. Here his chief collaborator was his friend and former pupil, Meyerhoffer. Often in conjunction with younger men, they studied the physical chemistry of the Stassfurt salt deposits, and similar phase-rule problems.

Such work, though of much general and special interest, is not to be placed on a par with van't Hoff's former achievements. It is true that in plan and in performance it may be taken as a model for an investigation on the grand scale, yet one cannot but entertain the feeling that a lesser man than van't Hoff, for example, his own countryman, Bakhuis Roozeboom, might have carried it to an equally successful conclusion. The conception of solid solutions (1890) is van't Hoff's last contribution to novel chemical ideas.

Van't Hoff had now more leisure, not only for practical research, but for travel. He has left an interesting journal of his impressions of America in 1901. In December of the same year he journeyed to Stockholm to receive the first Nobel Prize for Chemistry; and it may be recalled that he delivered the Raoult Memorial Lecture here in 1902.

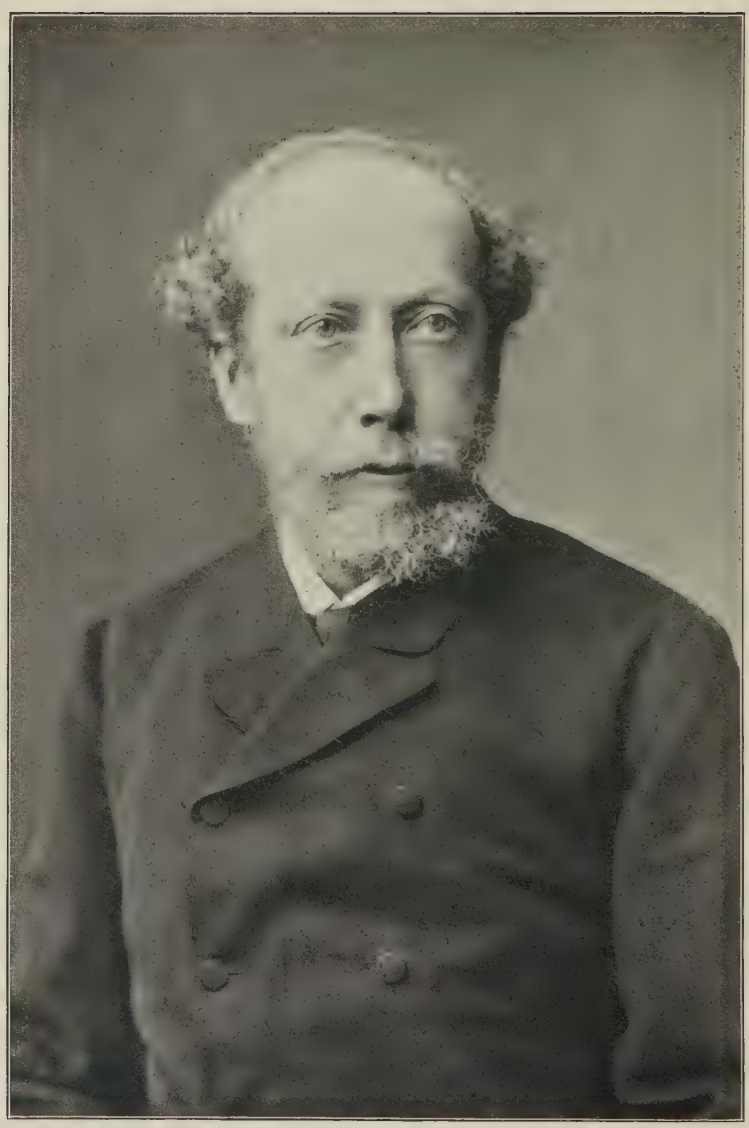
The death of Meyerhoffer in 1906 affected him deeply, and later in the same year his own health began to give way. He himself writes: "My health, almost invariably good, seemed in the summer of 1906 to be even better than usual. In early spring I had visited the neighbourhood of Vesuvius at the time of the eruption, and returned home rejuvenated. Hay-fever, for many years my bugbear, had vanished, and it appeared as if my Bonn student days, with all their poetry, had, comet-like, returned. And yet I found in

all this something abnormal, and recalled to mind a saying of a former medical colleague, that a feeling of specially good health in one's later years is a bad omen. In October came the first indications of what six months later developed into an illness which for a time laid me aside from all work." From that date van't Hoff had to spare himself, a thing peculiarly distasteful to a man of his active mind and temperament. He brought his work on the salt-deposits to a close, and devoted himself to the lighter labour of revising some of his older books, and projecting new ones.

His last scheme of investigation was a study of the intimate nature of the chemical processes occurring in plants. To this end he began in 1909 a research on reversible enzymatic action, and published a preliminary account in the *Sitzungsberichte* of the Prussian Academy (October, 1909, and November, 1910). These admirable fragments show a last flash of van't Hoff's illuminating genius. The clearness of the theoretical conceptions, the simplicity of the experimental execution recall the best period of his activity. He proved that the action of the enzyme emulsin in the formation and decomposition of glucosides was that of an ordinary catalyst in accordance with the mass-action law, the rates of the reverse reactions alone being affected and the point of equilibrium remaining unchanged.

The last experiments were carried out in a small private laboratory which had been built for him on the Imperial Crown-lands at Dahlem. Here from time to time he was able to do a little work, but the progress of his malady slowly enfeebled him. The entry in his diary for December 11th, 1910, reads, "Article on 'Teaching and Research' finished: a last effort." On the evening of March 1st, 1911, he died peacefully.

With no great mathematical or experimental attainment, with no striking gift as a teacher, van't Hoff yet influenced and moulded the current thought, and even much of the practice, of chemistry for decades. He set out with a clear scientific ideal. Native inspiration and unflagging ardour in pursuit of this ideal led him to the discovery of principles of the widest and most far-reaching import. He was, in my judgment, the greatest chemical thinker of his generation. If any should dispute this judgment, I can only reply that our science is indeed favoured when such dispute is possible.



[*To face p.* 273.

LADENBURG MEMORIAL LECTURE.

Delivered on October 23rd, 1913.

By Frederic Stanley Kipping, D.Sc., Ph.D., F.R.S.

A meeting of this Society which is held to commemorate the life and work of a distinguished chemist is an occasion which we approach with mingled feelings. For although we have to deplore the loss of a great man, there remain with us the recollection of his high achievements, and the example of his life worthily devoted to the advancement of knowledge.

In the minds of all chemists now living, and of all those who, in the future, trace the development of the science of our time, the name of Ladenburg is, and always will be, closely associated with the chemistry of those interesting and wonderful products of nature's laboratory, the vegetable alkaloids.

The study of some of the difficult problems presented by these complex compounds formed the main part of the experimental work of the man whose memory we honour to-day. It was a task which might well have deterred the boldest and the most sanguine spirit; but by him it was faced with persistent industry and indomitable perseverance, and brought to an issue the brilliancy of which few could have foreseen. The synthesis of *dl*-coniine, followed by the resolution of the synthetic alkaloid into its optically active components, the culminating point of these researches, was perhaps the greatest of Ladenburg's successes.

It is sometimes possible to trace the steps by which an explorer of the secrets of nature has passed from one dark region to yet another even more obscure; sometimes, however, not a single foot-print remains to mark the track. In Ladenburg's case, the study of the nitrogenous products of the vegetable kingdom was preceded by an investigation of the compounds of that element which dominates the mineral world; the derivatives of benzene seem to have formed the bridge by which he crossed the gulf between those two so widely different tracts, but there is no clear record of the inspiration by which he was guided. It may have been that, while searching among the musty archives of the days long past, during the preparation of his historical work on the development of chemistry, he became fascinated by the mystery surrounding the nature and the action of those potent poisons which are elaborated by plants; the product of a common weed, even such as the deadly nightshade, which could either enhance the charms of a fair lady or lead to delirium and death, might well appeal to the imagination

of the youthful chemist, and become to him an object of absorbing scientific interest.

However this may have been, the more difficult part of the task, with which I have been entrusted, is not that of tracing Ladenburg's progress as an investigator; it is that of passing in brief review the leading personal incidents of his distinguished career.

Happily, some of the difficulties ordinarily associated with such a task have in this case been dispelled by the existence of an authentic account of many of these events from his own pen. Towards the close of his life, he suffered from severe bodily ailments, which prevented him from carrying out his official duties. It was then that, at the suggestion of his friends, and as a means of intellectual recreation, he undertook the preparation of a short autobiography. A copy of this work was very kindly lent to me by Ladenburg's second son, Dr. Rudolph, and from this authoritative source most of the following particulars have been taken.

Born of Jewish parents on July 2nd, 1842, at Mannheim, in the Grand Duchy of Baden, Albert Ladenburg was one of a family of eight, of whom, however, five died quite young. Although his parents were in a good position (his father was a Rechtsanwalt), and lived in a large, many-roomed house, he and his brother and sister were brought up in the old-fashioned way, and were seldom allowed in the apartments of their father and mother.

The school to which he was sent was one in which little Latin was taught, and no Greek; one reason for this choice was that his father's experience of the classical education given at the Gymnasium had been that it took away all desire for work. From school he went on to the Polytechnicum at Karlsruhe, where he applied himself industriously to the study of mathematics, modern languages, machine construction, and other subjects, and, as he himself says, tried to make good a part of what he felt had been wanting in his earlier education.

In 1860, at eighteen years of age, he went to Heidelberg, where he attended lectures at the University, and worked very diligently at home. At first he had the idea of specialising in mathematics; but he also studied chemistry under Bunsen, and later, physics, under Kirchhoff. The lectures of Bunsen, however, proved so inspiring that Ladenburg very soon went over to chemistry, and spent the livelong day in Bunsen's laboratory. Here he met, among others, C. Graebe, H. Wichelhaus (who remained his close friend for many years), C. Liebermann, Soret, and W. Preyer. He also became acquainted with Roscoe, who often visited Bunsen in those days.

During the winter session 1862–1863, Ladenburg studied in

Berlin, attending lectures by Magnus, Ranke, and others, and in the spring of 1863 he took the Ph.D. degree at Heidelberg University, *summa cum laude*, in chemistry, physics, and mathematics.

Up to this time he had devoted himself principally to inorganic chemistry, but he now began to work with Carius, who, although *Ausserordentlicher Professor* in the University of Heidelberg, had to work in a small private laboratory outside. Here it was that Ladenburg carried out his first research work, which was on a new method of elementary organic analysis, and it was during this period that he made the acquaintance of Erlenmeyer, an acquaintance which resulted in a lasting friendship.

In the spring of 1865, Ladenburg decided to go to Ghent to work under Kekulé, who at that time was at the height of his scientific activity, and had just published his first paper on the structure of aromatic compounds. At Ghent he met Körner and Glaser, who were assistants to Kekulé; he also carried out two researches on benzene derivatives, one on the "Synthèse de l'acide anisique," the other, in conjunction with Fitz, on "Quelques derivés de l'acide paraoxybenzoique." Except for the opportunities of intercourse with Kekulé, and with the staff and students of the laboratory—opportunities which Ladenburg prized very highly—he found life in Ghent very dull, and after a short visit to London, where he met Frankland, he proceeded to Paris. Acting on Kekulé's advice, he there interviewed Berthelot, and asked for permission to become one of Berthelot's pupils; his request was granted forthwith, but when he proceeded to inquire where he should work, he was shown a large, empty room, devoid of all fittings, of which he would be the sole occupant.

Dissatisfied with the prospect of sacrificing a considerable proportion of his time in Paris to the fitting up of this room, and of having no fellow-students with whom he could converse, in order to improve his French, he obtained an introduction to Wurtz, who was professor in the Institut de chimie, and started work in his laboratory. It was there that Ladenburg met Friedel, Caventou, Naquet, A. Gautier, and others; from Wurtz's laboratory he published with Leverkus a paper "Ueber die Konstitution des Anethols."

At the beginning of the winter of 1866, after spending a few months in Germany, he went, at Friedel's invitation, to work in the École des mines, where, with Friedel, he began that important series of researches on derivatives of silicon to which reference will be made again. Shortly after the commencement of this work, he was very seriously hurt by an explosion, so seriously, in fact, that his parents, who happened to be in Paris at the time, were

hardly allowed to see him. The cause of this explosion is not mentioned in his *Lebenserinnerungen*, but judging from the work described in the first paper published by himself and Friedel, it was very probably the ignition of a mixture of the vapour of silicochloroform and air. Whatever the cause of the accident may have been, as soon as he was better, he set to work again and remained in Paris during the whole of a very hot summer, in order to make up for the days lost during his temporary disablement.

Up to this time, apparently, he had not definitely chosen a profession, but now he decided to become a teacher. To this course his father consented, although he lacked faith in his son's ability. Having consulted Bunsen and Kopp in Heidelberg on the matter of his *Habilitation*, and having been informed that the original work which he had done would be accepted, Ladenburg went for a short period to Berlin, there to undertake a projected research with Wichelhaus. This collaboration led to no definite result, but his stay in Berlin was very pleasant; it gave him an opportunity of meeting Wallach, who was assistant to Wichelhaus, and also of renewing his acquaintance with Baeyer and Martius, both of whom he had previously met in Paris. At the instance of Wichelhaus, steps were then being taken to found the *Deutsche Chemische Gesellschaft*, and both Baeyer and Martius shared with Wichelhaus this important undertaking.

In January, 1868, Ladenburg successfully underwent the ordeal of his *Habilitation*, and having spent a short time in Paris, where he continued his work with Friedel, he returned to Heidelberg, in order to rent and equip a laboratory in which he could also lecture. In those days rooms were not available in the large institute occupied by Bunsen; and Erlenmeyer, Horstmann, W. Lossen, and all the chemistry *Privatdocenten* had their own laboratories outside.

At the beginning of the term, Ladenburg commenced his first course of lectures, the subject being the history of the development of chemistry during the last hundred years. He had composed the earlier lectures while he was in Paris, and later, when continuing the task at Heidelberg, he had the advantage of the advice and criticism of Erlenmeyer. It was the matter of these lectures, carefully revised, which was published in 1869 under the title, "Vorträge über die Entwicklungsgeschichte der Chemie in den letzten hundert Jahren," a comprehensive, lucid, and critical work, which passed through several editions. At the end of his four years as *Privatdocent* in Heidelberg, he was given the title of *Professor extraordinarius*. The award of this honour, it seems, had been delayed a year, a delay which Ladenburg regarded as a punishment for his having petitioned the Ministry, on behalf of

his colleagues and himself, to provide *Privatdocenten* with laboratories suitable to their work, and to allow them to attend the University lectures at nominal fees.

In 1872, he accepted, after some hesitation, the offer of the chair of chemistry in the University of Kiel. The prospects there were not attractive. On his first visit, the town itself, the University, and some of the public buildings, gave him the impression of wretchedness, an impression, however, which was afterwards modified. There was, moreover, no chemistry department; and although it was understood that one should be built and equipped in about three years, there was no place in which he could work in the meantime. Nevertheless, he finally decided to accept the professorship, and in 1873 he began to teach at Kiel in a temporary laboratory, which had been rapidly fitted up in a vacant dwelling house.

At first he had only a few students, and could give much time to his own work, although he was worried by frequently occurring committee meetings, at which there were long and acrimonious disputes among the professors, each of whom was eager to secure the best site for his own projected buildings. During this period of comparative freedom from his teaching duties, he was able to commence, in conjunction with various other chemists, the preparation of his "Handwörterbuch der Chemie," a work which was finally pubished in thirteen royal octavo volumes.

The new Chemistry Institute in Kiel, of which Ladenburg was appointed Rector in 1884, was not ready for occupation until the winter session of 1878–1879. Attracted by the fame of the professor, and by the lucidity and fire of his lectures, students came in rapidly increasing numbers, and soon his laboratory became crowded. While at Kiel he was responsible for passing more than twenty-five doctors of philosophy in chemistry, and it was there that he carried out many of his more important researches on the alkaloids, including the synthesis of coniine. Towards the end of his stay in Kiel, he suffered a very severe blow in the loss of his mother, to whom he was deeply attached.

In 1889, he was offered the professorship of chemistry in the University of Breslau. At first he decided to decline the call, as he found, on visiting the town, that it was devoid of all attractions, while the so-called laboratory was hardly worthy to be dignified by such a name. However, having obtained a promise that the buildings then in use should be immediately reconstructed, and that a large new Institute should very soon be erected, he accepted the chair, and took up his residence in Breslau.

At first he was very disappointed that only twenty-five students

came to work with him, and that his lectures were only very sparsely attended, but as time went on, and especially after the new Institute had been opened in 1897, the number of his students increased to such an extent that on his resignation of the chair in 1909, he had the satisfaction of having passed 160 doctors of philosophy in chemistry. Few could show such a splendid record, even in those days, when the stream of prospective German chemists was at its flood.

During his first twelve years at Breslau nothing occurred to diminish Ladenburg's mental or bodily activity, but from 1901 onwards, one great trouble quickly succeeded another. He lost his youngest son, who had been ill for many years; his relations with friends and colleagues were sorely embittered by a controversy arising out of an address entitled "Einfluss der Naturwissenschaften auf die Weltanschauung," delivered at the *Naturforscherversammlung* in Kassel in 1903; and in 1904 he himself became ill, and shortly afterwards had to undergo a serious operation. Although, after many months of suffering, he recovered sufficiently to be able to resume fitfully his academic duties, his health soon gave way again. The tragic loss of his eldest son, who was drowned in 1908; the death of his wife, after a most distressing illness; and his own serious ailments, led him in 1909 to tender his resignation. He died two years later, on August 15th, 1911, in his seventieth year.

A man, like Ladenburg, who, in spite of poor health, leaves a record so deeply graven on the roll of fame, must have been possessed of inexhaustible and indomitable will-power and untiring industry. Even as a youth, his devotion to his work led him to refuse the delights of a long tour in Switzerland in order to spend the time in Bunsen's laboratory; and it was by this spirit that the whole of his life was ruled.

The honours which were bestowed on him and which were earned by this stern self-sacrifice on the altar of science, were not confined to those which he received in Germany; for in addition to the title of *geheimer Regierungsrath*, the Rectorship of the University of Kiel, and the membership of the *Akademie der Wissenschaften* of Berlin, he was an Honorary and Foreign Member of this Society, a member of the *Académie des Sciences*, and correspondent for the chemistry sections of numerous other scientific societies; he was awarded the Hanbury Medal of the Pharmaceutical Society in 1902, and the Davy Medal of the Royal Society in 1907.

Well might these honours and the place which he had gained for himself in the scientific world afford him some consolation in the dark days of his closing years; but possibly they seemed to him of

little import in comparison with the glad memories of more than thirty years of happy wedded life.

His wife was Margarete, the eldest daughter of Pringsheim, professor of botany in the University of Berlin. He met her late in 1875, during a visit to the capital, and with him it was a case of love at first sight; he proposed the following Easter, and they were married on September 19th of the same year. They had three sons, of whom only one survives.

Except when writing of his relations and friends, for whom he expresses freely his deep love and affection, Ladenburg preserves in his recollections a dignified silence as to his own feelings, and a reserved modesty as to his own achievements. He does not even refer to his great "Handwörterbuch der Chemie," the completion of which must have given him profound satisfaction; nor is there a word to intimate the acute intellectual gratification which he must have felt when he had brought some important research to a successful issue. To a man of his devotion to science, however, the joy of adding a stone to the eternal edifice of truth must have been intense; and, though unrecorded, his feelings when he first glanced through the polarimeter tube containing his synthetic optically active coniine, might perhaps have been expressed in the words which Biot once addressed to Pasteur: "J'ai tant aimé les sciences dans ma vie, que cela me fait battre le cœur."

However great may have been Ladenburg's own satisfaction on that occasion, he hastened to share it with his wife, who happened to be away from Kiel at the time; the brief telegram, "Gretchen, es dreht," which he sent to her,* conveyed no doubt infinitely more than was expressed in those three words.

In spite of the reticence as to his own characteristics which pervades his *Lebenserinnerungen*, there are a few passages which throw dim sidelights on his personality. He was the kind of man we call resolute or stubborn, strong-willed or obstinate, according as his point of view agrees or disagrees with our own. When he felt himself in the right, he defended his position tenaciously, a course which involved him in litigation on more than one occasion, and which led him to publish a considerable number of polemical papers.

The unremitting attention which he gave to his academic duties left him but little time for relaxation; nevertheless, like so many of his race, he possessed musical talent of a high order, and cultivated this gift in his rare moments of leisure. In his early youth at Karlsruhe, he spent many hours at the piano; later at Heidelberg he played in quartets and other concerted music, and obtained

* Dr. Rudolf Ladenburg kindly gave me this information.—F. S. K.

a great mastery over his instrument. He was a great lover of Brahms, with whose compositions he had been made familiar by Frau Schumann, a frequent visitor at his father's house and his own. He would travel a long distance in order to hear a new work of this composer, and when at Kiel he considered it his duty to cultivate among his friends a taste for Brahms, whose music at that time was little known in the town. On several occasions he met Brahms, and had the intense pleasure of hearing that great genius interpret his own compositions.

This brief outline of Ladenburg's life, drawn by one who had not the honour of his acquaintance, must necessarily fail completely to give a picture of the living man. As this defect could not be remedied, the delineation of Ladenburg's character may be left to the more competent pen of one of his own countrymen and colleagues, the writer of the memorial published in the *Berichte*.

When in 1866 Ladenburg was invited by Friedel to go and work in Paris on compounds of silicon, only a few organic derivatives of that element were known; those containing a silicon atom directly united to a carbon atom could, in fact, be counted on the fingers of one hand. If this state of knowledge is contrasted with that which obtained in 1883, when Beilstein's "Handbuch der organischen Chemie" was first published, some idea may be gained of the progress which had been made during the intervening years. This great advance was principally due to those researches which, commenced with Friedel, were continued by Ladenburg alone, and which formed, not the very first, but one of the earlier chapters of the latter's scientific record.

The first joint communication, published in 1867 (*Annalen*, **143**, 118), contained an account of silicochloroform. Some ten years previously Buff and Wöhler had heated crystalline silicon in a stream of dry hydrogen chloride, and had obtained a liquid to which they had given the formula $Si_2Cl_3 + 2HCl$ (Si = 21); this formula was subsequently altered by Wöhler to $Si_6Cl_{10}H_4$ (Si = 14), but he recognised the fact that he had been unable to obtain the liquid in a pure state, and that consequently its formula was not definitely established. Friedel and Ladenburg prepared this compound in a state of purity, and proved it to have the molecular formula $SiHCl_3$; its further study led them to the discovery of several interesting and novel reactions. One of its derivatives, namely, triethyl orthosilicoformate, which was obtained by treating the trichloro-compound with ethyl alcohol, underwent a remarkable decomposition when it was warmed with sodium; the metal remained unchanged, but the ester was decomposed, giving pure silicomethane, SiH_4, and

an ester of orthosilicic acid, a change which is expressed by the following equation: $4SiH(OEt)_3 = SiH_4 + 3Si(OEt)_4$.

This reaction, which is comparable to the decomposition by heat of the lower acids of phosphorus into phosphine and orthophosphoric acid, passed into the text-books of inorganic chemistry as a method for the preparation of pure silicomethane, and the equation just given has certainly been committed to memory, for examination purposes, by many puzzled students, who had not the remotest idea of the nature of triethyl orthosilicoformate.

As silicomethane had not until then been prepared in a pure state, Friedel and Ladenburg established its composition, and found that the pure gas was not spontaneously inflammable in air at the ordinary temperature and pressure, but was so under lower pressures. In addition to silicochloroform, they investigated other purely inorganic silicon compounds, more particularly silicon oxychloride, $SiCl_3 \cdot O \cdot SiCl_3$, which they prepared by passing the vapour of silicon tetrachloride through a white hot porcelain tube (*Ber.*, 1868, **1**, 86); although unable to discover how this compound was produced, they proved that it reacted with alcohol, giving the ethoxy-derivative, $Si(OEt)_3 \cdot O \cdot Si(OEt)_3$, and with zinc ethyl at 180°, giving silicoethyl oxide, $SiEt_3 \cdot O \cdot SiEt_3$.

The only method available in those days for bringing about the direct union of silicon and carbon was to heat silicon tetrachloride with zinc alkyls in sealed tubes. By using sodium in conjunction with the zinc compound, Friedel and Ladenburg succeeded in bringing about the displacement of the chlorine by an alkyl group at much lower temperatures and without the use of sealed tubes (*Ber.*, 1870, **3**, 15). In this way they prepared triethyl orthosilicopropionate, $SiEt(OEt)_3$, from triethoxysilicic chloride, which was itself obtained by the interaction of silicon tetrachloride and ethyl alcohol.

This ester was not completely hydrolysed by alcoholic potash in the cold, and when boiled with a concentrated aqueous solution of the alkali, it gave a product which had only approximately the composition $EtSiO \cdot OH$. For the preparation of the pure acid the ester was heated in sealed tubes with acetic chloride, and the product, ethylsilicon trichloride, $SiEtCl_3$, was hydrolysed with water. Silicopropionic acid, $EtSiO \cdot OH$, was thus obtained as an amorphous powder; it was the first representative of the silicon analogues of the carboxylic acids. Although, later on, Ladenburg prepared silicoacetic acid, $MeSiO \cdot OH$ (*Ber.*, 1873, **6**, 1029), and silicobenzoic acid, $PhSiO \cdot OH$, and several compounds supposed to be of this type have been obtained in recent times, little is known of their nature: except for the fact that such acids give soluble potassium salts,

they are extremely inert, and behave in every respect differently from the carboxylic acids.

The discovery of silicopropionic acid raised in Ladenburg's mind a question which, some years afterwards, he attempted to solve (*Ber.*, 1872, **5**, 568), namely, whether the silicon which is contained in plants is in combination with carbon or is a constituent of a purely mineral silicate. This problem, apparently, is still awaiting solution.

The main object of the joint researches just referred to was to gain some information as to the extent of the analogy between compounds of silicon and carbon; to ascertain whether the new theories which were just then being developed in connexion with organic compounds could also be applied to the so-called inorganic elements, or whether, as some believed, these new theories were both "unnütz und verwirrend."

As a further step in this direction, Friedel and Ladenburg (*Bull. Soc. chim.*, 1867, [ii], **7**, 65) attempted the synthesis of a quaternary hydrocarbon, and succeeded in obtaining dimethyldiethylmethane, CMe_2Et_2, the first known compound of this type; the existence of this hydrocarbon proved that the carbon atom, like the silicon atom in Friedel and Craft's tetraethylsilicane, $SiEt_4$, could unite directly with four hydrocarbon radicles.

They next tried to obtain a compound in the molecule of which two silicon atoms were directly united, as are the carbon atoms in ethane; after many fruitless attempts they finally succeeded (*Bull. Soc. chim.*, 1869, [ii], **12**, 92; *Annalen*, 1880, **203**, 241) in preparing silicoethane, $SiEt_3{\cdot}SiEt_3$, in the following manner: Silicon tetraiodide was heated with molecular silver at about 300°, and was thus converted into the hexaiodide, Si_2I_6 (from which the corresponding bromide, Si_2Br_6, and chloride, Si_2Cl_6, were prepared). The hexaiodide was hydrolysed with ice-cold water, yielding an amorphous product, silico-oxalic acid, $\begin{matrix}SiO{\cdot}OH\\ |\\ SiO{\cdot}OH\end{matrix}$, which showed an interesting behaviour; when heated in the air, the acid was decomposed into silica and hydrogen; when warmed with potassium hydroxide it gave potassium metasilicate with evolution of hydrogen:

$$H_2SiO_4 + 4KOH = 2K_2SiO_3 + 2H_2O + H_2.$$

The interaction of silicon hexaiodide and zinc ethyl took place very readily, giving a colourless liquid, boiling at 250—253°, which was proved to be the desired compound, hexaethylsilicoethane, $SiEt_3{\cdot}SiEt_3$.

During the preparation of triethyl silicoformate from triethylsilicic chloride, Friedel and Ladenburg had observed the formation

of diethoxydiethylsilicane, $SiEt_2(OEt)_2$, as a by-product. This observation led Ladenburg to study the action of zinc ethyl and sodium on ethyl orthosilicate, $Si(OEt)_4$. In a series of papers (*Ber.*, 1871, **4**, 727, 901; 1872, **5**, 565, 1081) he showed that the ethoxy-groups in this ester might be successively displaced by ethyl radicles, giving the compounds $SiEt(OEt)_3$, $SiEt_2(OEt)_2$, $SiEt_3{\cdot}OEt$, and $SiEt_4$, as well as triethylsilicane, $SiEt_3H$.

The diethoxydiethyl derivative, $SiEt_2(OEt)_2$, could not be hydrolysed to the corresponding dihydroxy-compound with alcoholic potash, but when heated with acetyl chloride in sealed tubes it gave the halogen derivatives $SiEt_2(OEt)Cl$ and $SiEt_2Cl_2$; the latter, with water, yielded a thick syrup, which Ladenburg regarded as silicon diethyl ketone, or oxide, $SiEt_2O$, but the analytical results did not agree well with those required for this formula.

The monoethoxy-derivative was hydrolysed by hydriodic acid, but gave the oxide $SiEt_3{\cdot}O{\cdot}SiEt_3$; when heated at 180° with acetyl chloride, it was converted into silicoheptyl chloride, $SiEt_3Cl$, which, with ammonia, gave silicoheptyl alcohol, $SiEt_3{\cdot}OH$. This was the first known silicon derivative of the alcohol type, and for this and analogous compounds, Ladenburg proposed the class name "silicole," corresponding with Kolbe's "carbinole."

A few silicon derivatives containing aromatic radicles were also prepared, as, for example, phenylsilicon trichloride, $SiPhCl_3$, which was obtained by heating silicon tetrachloride with mercuric phenyl (*Ber.*, 1873, **6**, 379). This trichloride and the ester, $SiPh(OEt)_3$, prepared from it, gave on hydrolysis products which seemed to be identical, and which were believed to be silicobenzoic acid, $PhSiO{\cdot}OH$.

Some thirty years later Ladenburg's thoughts again turned to these aromatic silicon compounds, and he prepared various derivatives of silicon tetraphenyl (*Ber.*, 1907, **40**, 2274), but apparently his attempts to sulphonate triphenylsilicol were not successful (*Ber.*, 1908, **41**, 966).

This short summary of Ladenburg's researches on silicon compounds can give little idea of the very great experimental difficulties with which he had to contend, and of the time which he must have devoted to these investigations. But in spite of the exacting character of this work, during its progress he was also able to study some organic compounds of tin.

The object here was not, as might have been expected, to establish some analogy between tin and silicon; it was to try and find out whether the molecule of a stannous compound contained one or two atoms of tin. In his opinion, the *ous* compounds of iron, manganese, chromium, and other metals contained two atoms of the

metal in their molecules (*Ber.*, 1869, **2**, 706), but experiments with certain inorganic iron, manganese, and tin compounds failed to give any evidence in support of this view. He therefore prepared "stanntriäthyl," a compound which had been obtained by Cahours, but the formula of which had not been established. This ethyl derivative was proved to have the composition, Sn_2Et_6, and the fact that two atoms of tin could unite directly was thus established, although the molecular structure of stannous compounds still remained unknown (*Ber.*, 1870, **3**, 353).

From the hexaethyl derivative Ladenburg prepared various other organic tin compounds; he showed that it was decomposed by iodine, giving tin triethyl iodide, $SnEt_3I$, from which, with the aid of sodium and bromobenzene, he obtained tin phenyltriethyl, $SnEt_3Ph$ (*Ber.*, 1871, **4**, 17). He also found (*Ber.*, 1871, **4**, 19) that the hexaethyl compound underwent the following interesting decompositions:

$$Sn_2Et_6 + 2EtI = 2SnEt_3I + C_4H_{10}.$$

$$Sn_2Et_6 + 2CH_2Cl{\cdot}CO_2H = 2SnEt_2Cl_2 + 2CO_2 + 2C_2H_6 + C_4H_{10}.$$

A much more important chapter of Ladenburg's work is that containing his numerous contributions, both theoretical and practical, on benzene and its derivatives. That a young and enthusiastic chemist, who had worked in Kekulé's laboratory, would take an active part in the solution of the many interesting problems suggested by the theory of the structure of benzene was, of course, only to be expected; it was merely a question of how far his own efforts would meet with success.

As a matter of fact, of the many who assisted in the examination of the fundamental propositions of the aromatic theory, few played a more prominent part than Ladenburg, or brought perspicacity and critical acumen of a higher order to the discussion of the experimental data. His first researches on aromatic compounds, carried out in Kekulé's laboratory and published in 1866–1867, have already been mentioned. During the next two years, although fully occupied with silicon compounds in the laboratory, his mind was evidently running on the aromatic theory, and as early as 1869 he contributed a paper in which he had the temerity to criticise Kekulé's formula, and to suggest alternatives, among which occurred the now well-known prism formula, originally put forward by Claus.

In this paper (*Ber.*, 1869, **2**, 272) Ladenburg showed that whereas, according to Kekulé's formula, the positions 1 : 2 and 1 : 6 must be, and the positions 1 : 3 and 1 : 5 may be, different, certain experimental data of Hübner and Petermann pointed strongly to the contrary conclusion, namely, that in the benzene

nucleus there are two hydrogen atoms which are symmetrically situated with respect to a third such atom. The argument was as follows: *m*-Bromobenzoic acid gives two bromonitrobenzoic acids, which, on reduction, are converted into the same aminobenzoic acid. The nitro-groups in the bromonitro-acids must have displaced two hydrogen atoms, which are differently situated with regard to the bromine atom, but identically situated with respect to the carboxyl group. Therefore either the position 1 : 2=1 : 6, or 1 : 3=1 : 5.

A few years later (*Ber.*, 1872, **5**, 322) he discussed the isomerism of benzene derivatives. The view that only three di-substitution products could be obtained was at that time supported by negative evidence only; no more than three such isomeric compounds had ever been prepared. From data established by Carstanjen (*J. pr. Chem.*, 1871, [ii], **3**, 50) in an experimental investigation of hydroxythymoquinone, Ladenburg not only deduced important conclusions regarding the symmetry of the benzene molecule, but also argued from Carstanjen's facts that only three di-substitution products of benzene were theoretically possible.

Two papers on pentachlorobenzene (*Ber.*, 1872, **5**, 789; 1873, **6**, 32) may next be mentioned, as they illustrate the experimental skill with which Ladenburg overcame a very difficult practical problem.

Two pentachlorobenzenes had been described, the one by Otto, the other by Jungfleisch. As the result of a most laborious investigation, involving hundreds of fractional crystallisations (*Annalen*, 1874, **172**, 331), Ladenburg was able to show that the supposed isomerides did not exist, and that a statement which could not be reconciled with the "Gleichwertigkeit" of the six hydrogen atoms of benzene had no foundation in fact.

In his work on mesitylene, which was published shortly afterwards (*Ber.*, 1874, **7**, 1133; *Annalen*, 1875, **179**, 163), he proved that the three displaceable hydrogen atoms in this hydrocarbon were all "gleichwertig," and consequently that mesitylene was symmetrical trimethylbenzene.

The proof was as follows: Dinitromesitylene, which may be represented by the formula $C_6Me_3\overset{a}{H}\overset{b}{N}O_2\overset{c}{N}O_2$, was converted into nitromesidine, $C_6Me_3\overset{a}{H}\overset{b}{N}O_2\overset{c}{N}H_2$, by reduction, and the acetyl derivative of this base was transformed into dinitracetmesidine, $C_6Me_3\overset{a}{N}O_2\overset{b}{N}O_2\overset{c}{N}HAc$. This compound was hydrolysed, and the dinitroamino-derivative converted into a dinitromesitylene, $C_6Me_3\overset{a}{N}O_2\overset{b}{N}O_2\overset{c}{H}$, by Griess' method. The substance thus obtained

was identical with the original dinitromesitylene; therefore two of the displaceable hydrogen atoms, *a* and *c*, are "gleichwertig."

The nitromesidine, $C_6Me_3\overset{a}{H}\overset{b}{N}O_2\overset{c}{N}H_2$, obtained from the dinitromesitylene, $C_6Me_3\overset{a}{H}\overset{b}{N}O_2\overset{c}{N}O_2$, gave the mononitro-derivative, $C_6Me_3\overset{a}{H}\overset{b}{N}O_2\overset{c}{H}$, when the amino-group was displaced by hydrogen. The nitro-compound was then reduced to mesidine, acetylmesidine was nitrated, and the product was hydrolysed to a nitromesidine, $C_6Me_3\overset{a}{N}O_2\overset{b}{N}H_2\overset{c}{H}$, or $C_6Me_3\overset{a}{H}\overset{b}{N}H_2\overset{c}{N}O_2$; but since $a=c$, these formulæ are identical. Since, moreover, this nitromesidine was identical with that, $C_6Me_3\overset{a}{H}\overset{b}{N}O_2\overset{c}{N}H_2$, obtained from dinitromesitylene, $b=c$, and therefore $a=b=c$. He frankly recognised that the fact that mesitylene was symmetrical trimethylbenzene afforded strong evidence against the prism formula, and he concluded therefore that "there is at the present time no symbolic representation of benzene which satisfies all requirements."

Another paper which has become a classic is that in which Ladenburg showed that in the benzene nucleus there were at least four hydrogen atoms which were identically situated (*Ber.*, 1874, **7**, 1684). His proof, which is of such fundamental importance that it is given in most of the test-books of organic chemistry, was the following. Phenol, treated with phosphorus pentabromide, gave bromobenzene, from which, with the aid of sodium and carbon dioxide, benzoic acid was obtained. Now benzoic acid was known to give rise to three isomeric hydroxybenzoic acids, $C_6H_4(OH)\cdot CO_2H$; in each of these compounds the hydroxyl group must have displaced a different hydrogen atom from the benzene nucleus, and none of these hydrogen atoms was identical with that displaced by the hydroxyl group in the original phenol. All three hydroxybenzoic acids were converted into a phenol and carbon dioxide; the phenol thus obtained was in every case identical with the original compound.

The substance of Ladenburg's more important contributions to the chemistry of benzene is to be found in his "Theorie der aromatischen Verbindungen," published in 1876, a few years after he went to Kiel. In this monograph he gave a critical review of the position of the aromatic theory at that time, and also did a great service to chemistry by drawing attention to the importance of Körner's method for the orientation of benzene derivatives.

Various other researches on aromatic compounds, including those on the aldehydine bases (*Ber.*, 1878, **11**, 590, 1648; see also *Ber.*, 1878, **11**, 1653, 1656), were carried out between 1876 and 1878,

but in the following year he began his study of the alkaloids and related compounds, a task which, with its side issues, occupied him almost exclusively during the rest of his working life.

In those days there were known various vegetable products, which were used in medicine for different purposes, but had in common the remarkable property of dilating the pupil of the eye. Among these alkaloids were belladonine and atropine, obtained from the deadly nightshade (*Atropa belladonna*), henbane, or hyoscyamine, from *Hyoscyamus niger*, duboisine, from *Duboisia myoporoides*, and daturine, from *Datura strammonium*. The only one of these substances that had been investigated other than very superficially was atropine; Lossen had shown that this base was hydrolysed by concentrated hydrochloric acid, giving tropine and tropic acid:

$$C_{17}H_{23}O_3N + H_2O = C_8H_{15}ON + C_9H_{10}O_3;$$

from tropic acid, atropic acid, $C_9H_8O_2$ (and isatropic acid) had been obtained, and atropic acid had been reduced to hydratropic acid, $C_9H_{10}O_2$.

Ladenburg first succeeded in preparing atropine from its decomposition products by evaporating a dilute hydrochloric acid solution of tropine with tropic acid (*Ber.*, 1879, **12**, 941); he found that this artificial atropine was identical with the natural product in every respect, including its physiological action.

He then showed that tropine reacted with other organic acids in a similar manner, in presence of hydrochloric acid, giving compounds which he named tropeines (*Ber.*, 1880, **13**, 1081; 1882, **15**, 1025); of these, the product from tropine and mandelic acid, phenylglycolyltropeine, or homatropine, $C_{16}H_{21}O_3N$, had a mydriatic action not quite so strong as, but much more rapid than, that of atropine; homatropine, moreover, was less poisonous than atropine. This partially synthetic alkaloid found application in ophthalmic surgery.

The results of the further investigation of atropine were published in numerous papers during 1880–1882, and were briefly as follows: Hydratropic acid, $C_6H_5{\cdot}CHMe{\cdot}CO_2H$, oxidised with permanganate (Ladenburg and Rügheimer, *Ber.*, 1880, **13**, 373), gave an acid, $C_9H_{10}O_3$, which was identical with the atrolactinic acid obtained by Fittig and Wurster (*Annalen*, 1879, **195**, 145) by treating atropic acid with hydrobromic acid and hydrolysing the product; this fact showed that atrolactinic acid had not the constitution $C_6H_5{\cdot}CH(CH_2{\cdot}OH){\cdot}CO_2H$ assigned to it by Fittig and Wurster, but $C_6H_5{\cdot}C(OH)(CH_3){\cdot}CO_2H$. Atrolactinic acid, heated with hydrochloric acid, was converted into atropic acid; the latter

combined with hypochlorous acid to form a chlorohydroxy-acid, from which tropic acid was obtained when the chlorine was displaced by hydrogen.

These results showed that tropic acid was not

$$C_6H_5\cdot C(OH)(CH_3)\cdot CO_2H,$$

as suggested by Fittig and Wurster, and that the relationship between the four acids just mentioned was as follows:

$C_6H_5\cdot CH<\begin{matrix}CH_3\\CO_2H\end{matrix}$ (I.) Hydratropic acid.

$C_6H_5\cdot C(OH)<\begin{matrix}CH_3\\CO_2H\end{matrix}$ (II.) Atrolactinic acid.

$C_6H_5\cdot C\lessdot\begin{matrix}CH_2\\CO_2H\end{matrix}$ (III.) Atropic acid.

$C_6H_5\cdot CH<\begin{matrix}CH_2\cdot OH\\CO_2H\end{matrix}$ (IV.) Tropic acid.

The synthesis of tropic acid was then accomplished in conjunction with Rügheimer (*Ber.*, 1880, **13**, 2041). Acetophenone dichloride, boiled with potassium cyanide in alcoholic solution, gave the compound $C_6H_5\cdot CMe(OEt)\cdot CN$, which, on hydrolysis, was converted into the acid $C_6H_5\cdot CMe(OEt)\cdot CO_2H$; the latter, with concentrated hydrochloric acid, gave atropic acid (III), from which tropic acid was prepared in the manner described above.

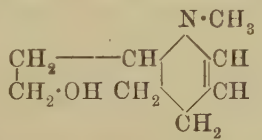
The determination of the constitution of tropine, the other decomposition product of atropine, was a much more difficult task, which Ladenburg attacked with great vigour. He found that when tropine, $C_8H_{15}ON$, was heated with concentrated hydrochloric acid, it was converted into tropidine, $C_8H_{13}N$ (*Ber.*, 1879, **12**, 944; 1880, **13**, 252); when heated with hydriodic acid, it gave an iodide, $C_8H_{15}NI_2$ (*Ber.*, 1881, **14**, 227), which, on reduction with zinc and hydrochloric acid, yielded hydrotropidine, $C_8H_{15}N$ (*Ber.*, 1883, **16**, 1408). When distilled with soda-lime, tropine gave methylamine, trimethylamine, hydrogen, and a hydrocarbon which was suspected to be valerylene, but its nature was not established (*Ber.*, 1881, **14**, 227).

As these results seemed to indicate that tropine was a derivative of a reduced pyridine or an oxidised piperidine nucleus, he prepared various alkylpiperidine derivatives, among others, *N*-propyl- and *N-iso*propyl-piperidine, and tried to convert these compounds by oxidation and other means into a base, which might prove to be identical with tropine or tropidine (*Ber.*, 1881, **14**, 1342). These experiments having failed, and the degradation of tropine by distillation with soda-lime having given such poor results, he next applied to this base a method which had been recently discovered by Hofmann, the now well-known process of exhaustive methylation.

From tropine and methyl iodide he obtained an iodide of methyltropine, $C_9H_{17}ON$, and found that this base was decomposed by

potassium hydroxide, giving dimethylamine (*Ber.*, 1881, **14**, 2126). Methyltropine, on further methylation, gave dimethyltropine iodide, from which by distillation, he obtained trimethylamine, an oil, $C_7H_{10}O$, which he named *tropilene*, and a hydrocarbon of the composition C_7H_8, which he called *tropilidene* (*Ber.*, 1881, **14**, 2403); this hydrocarbon seemed to be identical with that which he had previously obtained from tropine.

The composition and properties of tropilene led Ladenburg to conclude that this compound was related to suberone; he oxidised it with nitric acid, and found that it gave an acid which was probably normal adipic acid (*Ber.*, 1882, **15**, 1028). At the same time he discovered another very important fact, namely, that tropidine hydrobromide, heated with bromine at 170—180°, gave ethylene dibromide and dibromomethylpyridine; with excess of bromine it gave ethylene dibromide and dibromopyridine (*Ber.*, 1882, **15**, 1140). From all these observations he concluded that tropine was probably a methylpiperidine or methylpyridine derivative of the following constitution (*Ber.*, 1882, **15**, 1028):



While these experiments were in progress he also examined several of the other mydriatic drugs; in the course of this work he showed that duboisine and daturine were probably identical with hyoscyamine, that belladonine probably contained atropine, and that hyoscyamine and atropine were very closely related, so closely, in fact, that atropine could be synthesised from the decomposition products of hyoscyamine.

About 1882, Ladenburg's direct study of these mydriatic alkaloids gave place to his synthetic work on piperidine and pyridine derivatives. The main object of these researches was, no doubt, the synthesis of tropine, since he thought that this base was related to pyridine in the manner shown above.

The first important step in these synthetical experiments was the discovery that pentamethylenediamine could be obtained by the reduction of trimethylene dicyanide with zinc and hydrochloric acid (*Ber.*, 1883, **16**, 1149). This base, heated with sodium hydroxide, gave a compound, $C_5H_{11}N$, which seemed to be piperidine, and the identity of the synthetic base with that obtained from pepper was fully established by Ladenburg and Roth (*Ber.*, 1884, **17**, 513). As the yield of pentamethylenediamine in the above process was very unsatisfactory, Ladenburg devised a better

method for the preparation of the base, which consisted in reducing the dicyanide with sodium and alcohol (*Ber.*, 1885, **18**, 2956); he also showed that the hydrochloride of the diamine was converted into piperidine and ammonium chloride when it was distilled; as this change was evidently no far-reaching decomposition, the synthesis of piperidine in this way established the constitutional formula at that time assigned to that base.

While this synthesis of piperidine was in progress, he studied the behaviour of pyridine ethiodide at high temperatures (*Ber.*, 1883, **16**, 1410), and found that it gave ethylpyridine hydriodide when it was heated, by intramolecular change, just as the *N*-substituted anilines were known to give homologues of that base (Hofmann). He proved that the product contained γ-ethylpyridine by oxidising a fraction of it to *iso*nicotinic acid (*Ber.*, 1883, **16**, 2059), and also showed later (*Ber.*, 1885, **18**, 2961) that α-ethylpyridine and αγ-diethylpyridine were also produced, together with the γ-ethyl derivative, when pyridine ethiodide was heated.

It was now possible to obtain derivatives of pyridine from that base itself; in order to convert these compounds into the corresponding piperidine derivatives, Ladenburg investigated a method described by König for the reduction of pyridine to piperidine with zinc and hydrochloric acid, but he was unable to obtain any piperidine. He next tried reduction with sodium and alcohol, a process used by Wischnegradsky, and by a suitable improvement of this method, he was able to reduce coal tar picoline almost completely. In this way he obtained α-methylpiperidine, mixed with the β-compound, the first homologues of piperidine, excluding the *N*-derivatives, which had been prepared (*Ber.*, 1884, **17**, 388). He also reduced his γ-ethylpyridine to the piperidine derivative, and found that the latter had an odour of coniine.

This observation and the results of Hofmann's work, which had shown that coniine was in all probability α-propylpiperidine, led Ladenburg to attempt the synthesis of the last-named compound. With this end in view, he heated pyridine propiodide, and obtained a mixture of bases; one of these compounds gave, on oxidation, pyridine-γ-carboxylic acid, and seemed to be γ-propylpyridine; the other could not be obtained in a state of purity. The pure and the impure isomerides were separately reduced to piperidine derivatives; these compounds resembled coniine, but neither was identical with the latter. Immediately afterwards, with Schrade, he prepared α- and γ-*iso*propylpyridine in a similar manner from pyridine *iso*propiodide (*Ber.*, 1884, **17**, 1121). As these two compounds, like the supposed propyl derivatives, could not be completely separated by distillation, he converted the crude bases into the

corresponding piperidine derivatives by reduction with sodium and alcohol (*Ber.*, 1884, **17**, 1676), and then purified the latter with the aid of their platinichlorides.

The α-*iso*propylpiperidine thus obtained in a pure condition was carefully compared with coniine, and found to be remarkably similar to that base in all its properties, including its physiological action; the observed differences might be due merely to the optical inactivity of the synthetical base.

It was then found (*Ber.*, 1885, **18**, 1587) that the α- and γ-*iso*propylpyridines and also the supposed corresponding propyl derivatives could be completely purified with the aid of their platinichlorides; in each case the base of lower boiling point gave on oxidation picolinic acid, and was therefore the α-derivative, whilst the isomeride gave *iso*nicotinic acid, and was therefore the γ-derivative.

The pure α-pyridine bases (propyl and *iso*propyl) were carefully compared with conyrine, which Hofmann had obtained by heating coniine hydrochloride with zinc dust, and had shown to be either α-propyl or α-*iso*propylpyridine. They both differed from conyrine. Therefore, either the difference was merely due to stereoisomerism, or else the two synthetical bases must both be *iso*propylpyridine. The latter alternative was proved to be the true one; when pyridine propiodide was heated in order to convert it into propylpyridine, the *n*-propyl was transformed into the *iso*propyl group.

Since it had thus been proved that conyrine must be α-propylpyridine, Ladenburg attempted to prepare this base from pyridine allyl iodide, but obtained *iso*propylpyridine in place of the desired propyl compound (*Ber.*, 1885, **18**, 1587). Next he tried to condense picoline with paracetaldehyde in the presence of zinc chloride (*Ber.*, 1886, **19**, 439), a reaction which Jacobsen and Reimer had applied to obtain benzylidenequinaldine from quinaldine and benzaldehyde. In this way he obtained only very small quantities of an oily base, but the product had an odour of conyrine, and on analysis seemed to be allylpyridine. On reduction with sodium and alcohol, it gave a base having properties similar to those of coniine. These experiments were repeated with larger quantities of material (*Ber.*, 1886, **19**, 2578); 380 grams of picoline were treated in sealed tubes, and 45 grams of allylpyridine were obtained; the product was proved to be the α-derivative by oxidising it to picolinic acid, and was reduced to propylpiperidine; the latter was oxidised by Hofmann's method (*Ber.*, 1884, **17**, 825) to a base, which was found to be identical with conyrine. The synthetical propylpiperidine was finally converted into the acid tartrate, and the solution of the latter was seeded with a crystal of coniine acid tartrate; the crystal-

line deposit was decomposed with potassium hydroxide, and the liberated base was found to be dextrorotatory. The complete identity of the synthetical base with coniine, obtained from the hemlock, was then fully established; the alkaloid which had caused the death of the wisest of men was the first to succumb to the synthetic skill of the chemist!

This synthesis of coniine was accomplished in 1886, and for nearly twenty years afterwards Ladenburg continued his researches with undiminished activity. During this period he was occupied to a great extent with various issues arising out of his earlier work; it will therefore be more convenient to deal with the discoveries of this period under certain definite headings rather than to consider them in strict chronological sequence.

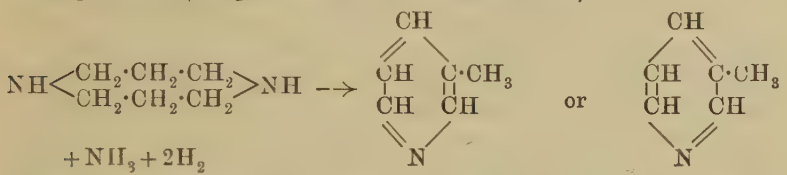
His studies of the diamines may be first considered (*Ber.*, 1886, **19**, 2585). He showed that his synthetical pentamethylenediamine was identical with cadaverine, a base isolated by Brieger from putrefying flesh. Tetramethylenediamine (*Ber.*, 1886, **19**, 780; 1887, **20**, 442) was converted into pyrrolidine, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>\!NH$, by the same method as that by which piperidine had been obtained from pentamethylenediamine, and pyrrolidine was also synthesised by reducing succinimide with sodium and alcohol (*Ber.*, 1887, **20**, 2215). The action of heat on ethylenediamine hydrochloride resulted in the formation of a base (*Ber.*, 1888, **21**, 758; 1890, **23**, 3740; 1891, **24**, 2400), which is now well known as piperazine.

$$NH\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>\!NH.$$

By the distillation of ethylenediamine hydrochloride with sodium acetate he obtained a base, lysidine, $\begin{matrix}CH_2\cdot NH\\ |\\ CH_2\text{---}N\end{matrix}\!\!>\!C\cdot CH_3$ (*Ber.*, 1894, **27**, 2952), identical with a compound prepared by Hofmann (*Ber.*, 1888, **21**, 2332) in an analogous manner. Lysidine, like piperazine, formed with uric acid a salt which was very readily soluble in water (*Ber.*, 1894, **27**, 2952), and clinical experiments, carried out at Ladenburg's suggestion, showed that a case of acute, and also one of chronic arthritis were both quickly cured by large doses of this base.

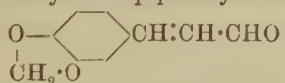
The action of heat on trimethylenediamine hydrochloride resulted, not only in the formation of trimethyleneimine, $CH_2\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>\!NH$, but also in the production of two picolines (*Ber.*, 1890, **23**, 2727); the production of these two pyridine derivatives was explained by assuming that the diamine first gave rise to a homologue of

piperazine, $NH<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>NH$, which then decomposed with formation of ammonia and two molecules of hydrogen, the eight-membered ring suffering disruption, and passing into a mixture of two β-picolines (compare also *Ber.*, 1890, **23**, 2688):



His investigations on pyridine derivatives led him to consider the orientation of the pyridinecarboxylic acids, and he pointed out the important fact that when a pyridinedicarboxylic acid was heated, the α-carboxyl group was always the first to be eliminated (*Ber.*, 1885, **18**, 2967). He isolated lutidine (*Ber.*, 1885, **18**, 913) and γ-picoline (*Ber.*, 1888, **21**, 285) from coal tar, and reduced these compounds to the corresponding piperidine derivatives. He showed that α-methyl- and α-ethylpiperidine could be resolved into their optically active components (*Ber.*, 1886, **19**, 2584, 2975), and that picolinic acid (*Ber.*, 1891, **24**, 640), as well as nicotinic and *iso*nicotinic acids (*Ber.*, 1892, **25**, 2768) could be reduced with sodium and alcohol to the corresponding piperidinecarboxylic acids. A summary of his work on pyridine and piperidine derivatives down to 1888 is given in the *Annalen*, 1888, **247**, 1.

The partial synthesis of piperine from piperidine and the chloride of piperic acid having been carried out by Rügheimer in the Kiel laboratory, the last link required to complete the chain was forged by Ladenburg and Scholtz (*Ber.*, 1894, **27**, 2958). Piperonal was condensed with acetaldehyde to piperonylacrolein,



and the latter, with the aid of sodium acetate and acetic anhydride, was converted into an acid,

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO_2H,$$

identical with the piperic acid obtained from piperine.

His analytical and synthetical experiments on tropine, which had been interrupted by his work on coniine, were continued intermittently down to 1902. Hydrotropidine hydrochloride, when heated, gave methyl chloride and a base, $C_7H_{13}N$, which he named norhydrotropidine; the hydrochloride of the latter, under similar conditions, gave α-ethylpyridine, together with a small quantity of

a hydrocarbon (*Ber.*, 1887, **20**, 1647). He also showed that tropidine was converted into tropine by treatment with hydrobromic acid (*Ber.*, 1890, **23**, 1780, 2225; 1902, **35**, 1159, 2295).

The resolution of tropic acid into its optically active components (Ladenburg and Hundt, *Ber.*, 1889, **22**, 2590) led to the preparation of optically active atropines, which were obtained by evaporating the active acids with a solution of tropine hydrochloride.

A large proportion of his work on tropine at about this time consisted of repeated but fruitless attempts to synthesise this elusive base. For this purpose, starting from piperidine derivatives, and using Hofmann's method (*Ber.*, 1885, **18**, 111), he prepared various tetrahydropyridine derivatives (*Ber.*, 1887, **20**, 1645) which he thought were related to tropine. He also prepared α-picolylalkine, $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot OH$, by the condensation of picoline and formaldehyde; this compound on distillation gave vinylpyridine, $C_5NH_4 \cdot C_2H_3$, which had a strong odour of conyrine, and on reduction was converted into α-pipecolylalkine,

$$C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot OH,$$

a base nearly related to tropine in composition and properties (*Ber.*, 1889, **22**, 2583). These synthetical experiments were, of course, predestined to fail, because they were founded on an erroneous view of the constitution of tropine; this fact, however, does not detract from the value of Ladenburg's positive results, which threw so much light on the nature of tropine and formed so excellent a foundation for the brilliant synthesis ultimately accomplished by Willstätter.

In another long series of papers, published between 1893 and 1906, Ladenburg follows up the discovery of a base which he regarded as a stereoisomeride of coniine. He found (*Ber.*, 1893, **26**, 854) that when coniine hydrochloride was distilled with a relatively small quantity of zinc dust, in addition to conyrine and unchanged coniine, it gave an optically active propylpiperidine, which differed from coniine in specific rotation and in certain other respects. He accounted for the existence of this base, which he named *iso*coniine, by assuming that the arrangement of the atoms or groups around the nitrogen atom was an asymmetric one, or, at any rate, that such an arrangement could modify the optical activity conditioned by the asymmetric carbon group (*Ber.*, 1896, **29**, 2718). By a method similar to that used in the conversion of coniine into *iso*coniine, he prepared from *d*-pipecoline an isomeric base, *iso*pipecoline (*Ber.*, 1894, **27**, 853), and by heating *l*-stilbazoline (*Ber.*, 1903, **36**, 3694), a compound obtained by resolving the reduction product of stilbazole, $C_5NH_4 \cdot CH{:}CH \cdot C_6H_5$, he prepared *iso*stilbazoline (*Ber.*, 1904, **37**, 3688). He made many

experiments to try and prove that these optically active *iso*-bases were definite compounds, and not mere mixtures in unequal proportions of the *d*- and *l*-isomerides (*Ber.*, 1895, **28**, 163; 1896, **29**, 2706; 1897, **30**, 485), and he also attempted unsuccessfully to obtain other nitrogenous compounds showing isomerism of the same nature (*Ber.*, 1896, **29**, 2710; 1897, **30**, 1582). In his last paper on this subject (*Ber.*, 1906, **39**, 2486), although he maintained the existence of *iso*coniine, the facts which he himself had established were so difficult to reconcile with his views that he was obliged to conclude that his own synthetical coniine was in reality the *iso*-base, and that the latter was only converted into natural coniine when it was strongly heated. An impartial verdict on this branch of Ladenburg's work may perhaps be implied by the statement that he is not the only chemist who has unsuccessfully devoted time and effort to prove the existence of asymmetry in tervalent nitrogen compounds.

In the course of his experiments on the resolution of piperidine derivatives and during his study of the active bases, Ladenburg made some important contributions to our knowledge of asymmetric compounds. He was the first to show that *dl*-bases could be resolved by the method discovered by Pasteur, and used by the latter for the resolution of *dl*-acids. He also showed that a lowering of temperature occurred when *d*- and *l*-coniine were mixed (*Ber.*, 1895, **28**, 163), whereas no change in temperature was observed in the case of certain other liquids of similar character, having the same specific gravity (*Ber.*, 1895, **28**, 1991). From these facts he argued that *d*- and *l*-coniine united to form a racemic liquid.

A general method for distinguishing solid racemic compounds from *dl*-mixtures was also put forward (*Ber.*, 1894, **27**, 3065), but as the result of adverse criticism, this method was modified as follows (*Ber.*, 1899, **32**, 864): "To decide whether an inactive, resolvable substance is a racemic compound or a mixture of active components, the solubility of the substance is determined with and without the addition of a small quantity of one of the active components (at the same temperature and in the same solvent). If the solubilities are different, the substance is racemic; if the same, it is an enantiomorphous mixture.

During some experiments on the resolution of β-pipecoline with the aid of tartaric acid, he found that when crystallisation occurred at about 100° the experiments failed, whereas at the ordinary temperature the *dl*-base was resolved (*Ber.*, 1894, **27**, 75); also, that the resolution of pyrotartaric acid (methylsuccinic acid) could be accomplished with the aid of strychnine (*Ber.*, 1895, **28**, 1170), but not with quinine. These results led him to conclude that the

dl-base formed with the *d*-acid and the *dl*-acid formed with the *l*-base a salt, one part of the molecule of which was racemic, the other part optically active. To such salts he applied the term half or partly racemic, which had been previously used by E. Fischer (*Ber.*, 1894, **27**, 3225) to denote mixtures, or compounds, of two optically active components which were similar but not enantiomorphously related.

The study of these partly racemic salts was described in numerous papers (*Ber.*, 1898, **31**, 524, 937, 1969; 1899, **32**, 50; 1903, **36**, 1649; 1907, **40**, 2279; 1908, **41**, 966), and a summary of the results was given in the *Annalen* (**364**, 227) in 1909. His experiments were chiefly directed towards obtaining evidence that the two types of partly racemic salts, namely, *d*A*l*B, *l*A*l*B, and *d*A*l*B, *d*A*d*B, were not merely mixtures, but were definite compounds. For this purpose he compared the properties of partly racemic strychnine *dl*-tartrate, *d*A*l*B, *l*A*l*B, with those of the *d*A*l*B and *l*A*l*B salts of strychnine and tartaric acid. He showed that the three compounds differed as regards the hydration of their crystals: also in solubility, specific gravity, specific rotation, and so on; and that the qualitative data could not be reconciled with the view that the partly racemic salt was a mere mixture of the *d*A*l*B and *l*A*l*B components. He also proved that partly racemic strychnine tartrate and brucine hydrogen tartrate had a transition temperature above which they underwent resolution. On the other hand, *dl*-pipecoline *d*-tartrate, which was deposited as a partly racemic salt at high temperatures, had a transition temperature below which it was resolved; *dl*-tetrahydroquinaldine hydrogen *d*-tartrate behaved in a similar minner. From all these results, Ladenburg concluded that the formation of partly racemic salts was a very general phenomenon; further, that the formation of such salts was strong evidence in support of the view that racemic compounds could exist in a dissolved state.

In 1898 he was able to break new ground with the aid of an apparatus for the liquefaction of air. He described various lecture experiments suitable for the illustration of low temperature effects (*Ber.*, 1898, **31**, 1968), and also determined the specific gravities of liquid air and other liquefied gases (*Ber.*, 1899, **32**, 46), as well as their boiling points (*Ber.*, 1899, **32**, 1818). He liquefied ozonised oxygen (*Ber.*, 1898, **31**, 2508), purified the ozone by fractional evaporation, and determined the density of this purified material with the aid of Schilling's apparatus; the purity of the samples, that is to say, the proportion of ozone which they contained, was checked by a titration of the iodine liberated from potassium

iodide by a known quantity of the gas. The density was thus found to be 1·456 (O=1).

In other papers (*Ber.*, 1898, **31**, 2830; 1900, **33**, 2283) dealing with this matter, he replied to objections which had been raised to his method on the grounds that he had used the formula O_3 for ozone in calculating the proportion of this gas in his samples. He then worked out the details of a process for estimating the ozone in a weighed quantity of ozonised oxygen with the aid of turpentine (*Ber.*, 1901, **34**, 631); he was thus able to determine the density of ozone without the use of potassium iodide. Later still (*Ber.*, 1901, **34**, 1184) he showed that the usual method for the estimation of ozone, with the aid of an acidified solution of potassium iodide, gave results which were 50 per cent. higher than the true values, but that correct estimations could be made if the gas were first absorbed in neutral solutions of potassium iodide, which were then acidified before titration.

The interesting question as to the relative positions of iodine and tellurium in the periodic system led Ladenburg to take up the study of the first-named element. He showed (*Ber.*, 1902, **35**, 1256) that silver iodide could be readily freed from silver chloride by repeated extraction with a concentrated solution of ammonium hydroxide until the solubility of the iodide became constant; he reduced the pure iodide with zinc and sulphuric acid, decomposed the zinc iodide which was thus formed with nitrous acid, and distilled the well-washed precipitated iodine in steam. He then determined the melting point, boiling point, and specific gravity of the pure halogen.

Shortly afterwards (*Ber.*, 1902, **35**, 2275) he made a series of determinations of the atomic weight of iodine, based on the conversion of silver iodide into silver chloride and a knowledge of the atomic weights of silver and chlorine. From the results of this work, he found the atomic weight, I=126·96, a value considerably higher than that (126·85) obtained by Stas, but which approximates very closely to that (126·92) which is given in the last report of the International Committee on Atomic Weights.

A list of Ladenburg's papers is given in the *Berichte* (1912, **45**, 3636).

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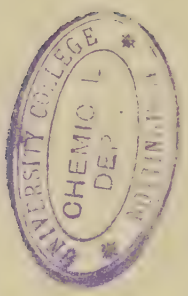
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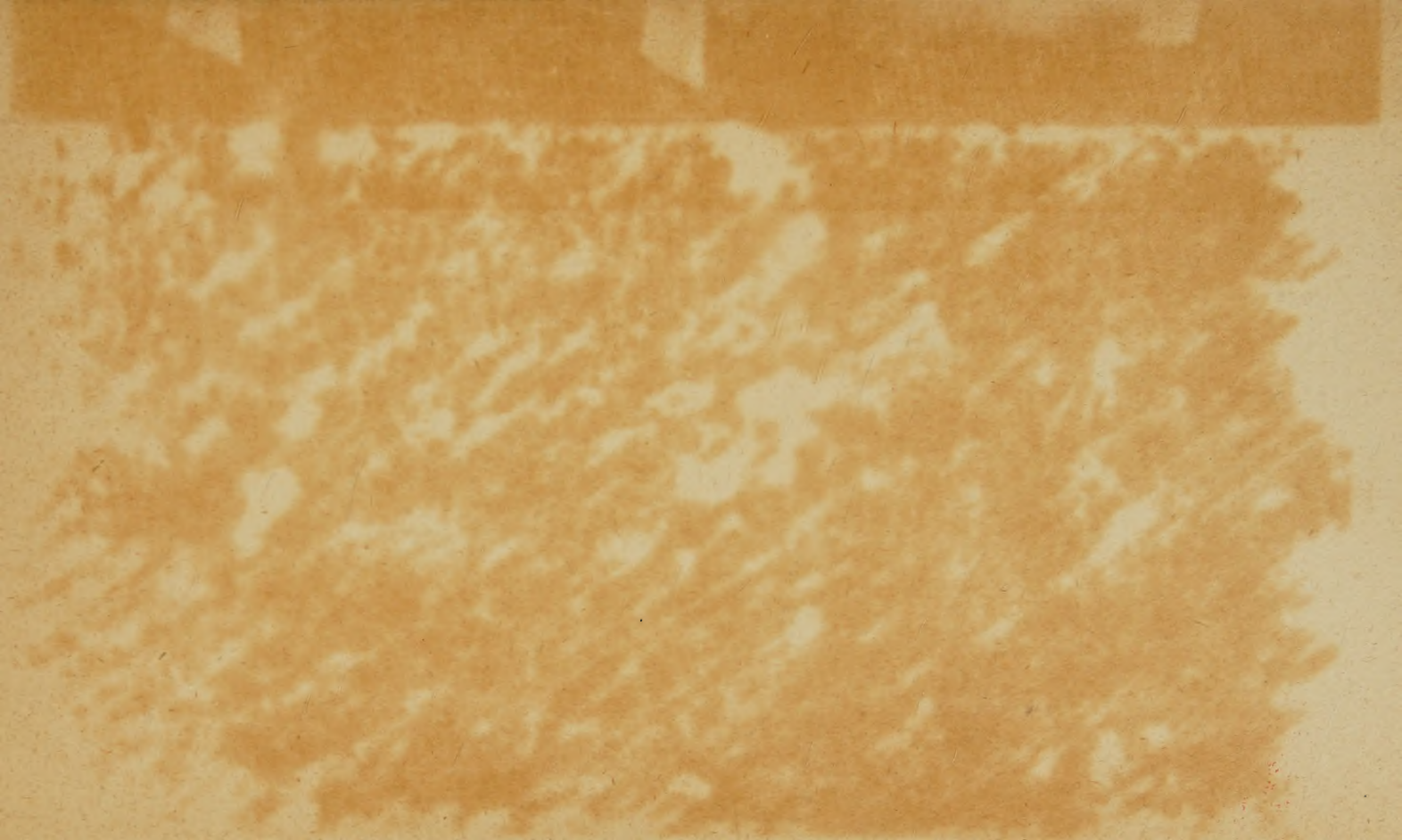

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